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THE TECHNOLOGY QUARTERLY

AND PROCEEDINGS OF THE SOCIETY OF ARTS

ERRATA

Volume 21, No. 2, page 174, Section V, line 2, for *platinum disk* read *platinum dish*. Page 176, Section VI, line 6, for *anion*, T^a_v, read *cation*, T^c_v

VOLUME XXI

BOSTON
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
1908

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THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY held its first meeting on April 8, 1862. By the act of incorporation, which was accepted at this meeting, the SOCIETY OF ARTS was created as a part of the Institute coördinate with the School of Industrial Science.

The objects of the Society are to awaken and maintain an active interest in the sciences and their practical applications, and to aid generally in their advancement in connection with the arts, agriculture, manufactures, and commerce. Regular meetings are held semi-monthly from October to May.

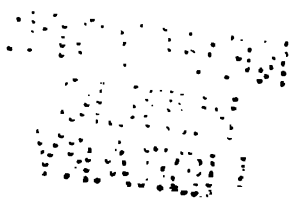
The Society discontinued the publication of the *Abstracts of Proceedings* in 1891, and since then has published its proceedings and the principal papers read at its meetings in the *Technology Quarterly*. The present volume contains the proceedings from October, 1907, to May, 1908, inclusive.

The *Quarterly* contains, also, the results of scientific investigations carried on at the Institute, and other papers of interest to its graduates and friends, and also a list of the publications of officers of the Institute, together with abstracts when possible.

Neither the Massachusetts Institute of Technology nor the SOCIETY OF ARTS assumes any responsibility for the opinions or statements in the papers.

NOTE

In view of the fact that the publication of the research work done at the Institute is now amply provided for in other ways, the Executive Committee of the Corporation have decided that the *Technology Quarterly* shall be discontinued after the completion of the present volume.



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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Society of Arts

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1908-1909

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Secretary of the Society of Arts

WALTER S. LELAND

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Editor of the Technology Quarterly

ROBERT P. BIGELOW

BY-LAWS.

Objects of the Society.

The objects of the Society are to awaken and maintain an active interest in the practical sciences, and to aid generally in their advancement and development in connection with arts, agriculture, manufactures, and commerce.

The Society invites all who have any valuable knowledge of this kind, which they are willing to contribute, to attend its meetings and become members. Persons having valuable inventions or discoveries which they wish to explain will find a suitable occasion in the Society meetings, subject to regulations hereafter provided; and while the Society will never indorse, by vote or diploma or other official recognition, any invention, discovery, theory, or machine, it will give every facility to those who wish to discuss the principles and intentions of their own machines or inventions, and will endeavor at its meetings, or through properly constituted committees, to show how far any communications made to it are likely to prove of real service to the community.

Section I. — Administration.

The immediate management and control of the affairs of the Society of Arts shall be exercised by an Executive Committee, consisting of the President of the Institute and the Secretary of the Society (who shall be members *ex officiis*), and five other members, who shall be elected by the Society of Arts at each annual meeting, to continue in office until other persons have been chosen in their place.

Sect. II. — Duties of the Executive Committee.

The Executive Committee shall elect its chairman, prescribe his duties, and, with the concurrence of the Treasurer of the Institute, fix his compensation when the interests of the Society require that

he should be paid for his services; they may invite any person to preside at any ordinary meeting who is well versed in the subjects to be discussed; they shall appoint the days and times of meeting, when not fixed by the Society, and determine the subjects to be considered at the meetings and the mode of conducting the discussions; they may, with the concurrence of the President of the Institute, make such arrangements for reporting and publishing the proceedings of the Society as they may deem best suited to advance its interests; they may receive moneys in behalf of the Society in aid of its objects, by subscription, donation, or bequest; they shall make a report of their doings to the Society at its annual meeting and at such other times as a report may be called for by a majority of the members present at any meeting; they shall also make a report of their doings to the President of the Institute prior to the annual meeting, and at such other times as the Corporation may require it. Three members shall constitute a quorum for the transaction of business.

Sect. III. — Duties of the President and Secretary.

1. It shall be the duty of the President of the Institute to preside at the annual and the special meetings of the Society, and also at its ordinary meetings when the Executive Committee does not invite a special chairman to preside.

2. It shall be the duty of the Secretary of the Society to give notice of and attend all meetings of the Society and of the Executive Committee; to keep a record of the business and orders of each meeting, and read the same at the next meeting; to keep a list of the members of the Society, and notify them of their election and of their appointment on committees; and generally to devote his best efforts, under the direction of the Executive Committee, to forwarding the business and advancing the interests of the Society. He shall also record the names of the Executive Committee attending each meeting.

Sect. IV. — Funds of the Society.

All the fees and assessments of members, and all moneys received by subscription, donation, or otherwise, in aid of the Society, shall be paid into the treasury of the Corporation, to be held and used for the objects of the Society under the direction of the Executive Commit-

tee, and shall be subject to the order of its Chairman, countersigned by the President of the Corporation.

Sect. V. — Meetings of the Society.

1. The annual meeting of the Society shall be held at the Institute on the second Thursday in May. The ordinary meetings shall be held semi-monthly, or whenever deemed expedient by the Society or by the Executive Committee, excepting in the months of June, July, August, and September.

2. If from any cause the annual meeting shall not have been duly notified or held as above required, the same shall be notified and held at such time as the Executive Committee may direct.

3. A special meeting of the Society may at any time be called by the Secretary on a written request of ten members. Twelve members of the Society shall constitute a quorum for the transaction of business.

Sect. VI. — Members and Their Election.

1. Members of the Society of Arts shall be of three kinds — Associate, Corresponding, and Honorary Members.

2. Candidates for Associate Membership shall be recommended by not less than two members, whose signatures shall be affixed to a written or printed form to that effect. Each nomination shall be referred to the Executive Committee, and when reported favorably upon by them, and read by the Secretary, may be acted upon at the same meeting; the election shall be conducted by ballot, and affirmative votes to the number of three-fourths of the votes cast shall be necessary for an election.

3. Corresponding and Honorary Members may be elected in the same way, on nomination by the Executive Committee.

4. Associate Members shall pay an admission fee of three dollars before being entitled to the privileges of membership, and an annual assessment of three dollars on the first of October of each year, this sum to include subscription to the *Technology Quarterly and Proceedings of the Society of Arts.*

An Associate Member who shall have paid at any one time the sum of fifty dollars, or annual assessments for twenty years, shall become a member for life, and be thereafter exempted from annual assessments

A member neglecting to pay his annual assessment for six months after being notified that the same is due shall be regarded as having withdrawn his membership, unless otherwise decided by the Executive Committee, which shall be authorized, for cause shown, to remit the assessments for any one year; and which shall moreover be empowered to exempt particular members from assessments whenever their claims and the interests of the Society make it proper to do so.

Sect. VII. — Election of the Executive Committee and of the Secretary.

1. At an ordinary meeting of the Society, preceding the annual meeting, a nominating committee of *five* shall be chosen, whose duty it shall be to nominate candidates for the Executive Committee, to post a list of the names selected in the office of the Secretary, and to furnish printed copies thereof to the members at or before the time of election.

2. At a meeting at which an election is to take place the presiding officer shall appoint a committee to collect and count the votes and report the names and the number of votes for each candidate, whereupon he shall announce the same to the meeting.

3. A majority of the votes cast shall be necessary to an election.

4. In the first organization under these By-Laws, the Executive Committee may be elected at an ordinary or special meeting.

5. Vacancies in the committee occurring during the year may be filled by the Society at an ordinary meeting.

6. The Secretary shall be elected by the Society, on nomination by the Executive Committee, at each annual meeting of the Society, or, in case of a vacancy during the session, at such other time as the Executive Committee may appoint; and he shall be reëligible in the same way at the pleasure of the Society.

7. The compensation of the Secretary shall be fixed from year to year by the Executive Committee with the concurrence of the Treasurer of the Institute.

Sect. VIII. — Committees of Arts.

1. The Members of the Society of Arts may be enrolled in divisions, under the following heads, according to the taste or preference of

the individual; each division to constitute a committee upon the subjects to which it appertains:

(1) On Mineral Materials, Mining, and the Manufacture of Iron, Copper, and other Metals.

(2) On Organic Materials — their culture and preparation.

(3) On Tools and Implements.

(4) On Machinery and Motive Powers.

(5) On Textile Manufactures.

(6) On Manufactures of Wood, Leather, Paper, India Rubber, and Gutta Percha.

(7) On Pottery, Glass, Jewelry, and works in the Precious Metals.

(8) On Chemical Products and Processes.

(9) On Household Economy; including Warming, Illumination, Water-Supply, Drainage, Ventilation, and the Preparation and Preservation of Food.

(10) On Engineering, Architecture, and Ship-building.

(11) On Commerce, Marine Navigation, and Inland Transportation.

(12) On Agriculture and Rural Affairs.

(13) On the Graphic and Fine Arts.

(14) On Ordnance, Firearms, and Military Equipments.

(15) On Physical Apparatus.

2. Any member may belong to more than one of the above-named Committees of Arts, but shall not at the same time be eligible as chairman in more than one.

3. It shall be competent for each Committee of Arts, of ten or more members entitled to vote, to organize; to elect annually in October, or whenever a vacancy shall occur, a chairman; to appoint its own meetings; and to frame its own By-Laws, provided the same do not conflict with the regulations of the Society of Arts.

Sect. IX. — Amendment and Repeal.

1. These By-Laws may be amended or repealed, or other provisions added, by a vote of three-fourths of the members present at any regular meeting of the Society; provided that such changes shall have been recommended and approved in accordance with the By-Laws of the Corporation (see extract from By-Laws of Corporation as

printed below) and presented in writing at a preceding meeting of the Society.

2. These By-Laws shall take effect immediately after their approval by the Corporation and adoption by the Society, and all previous By-Laws are hereby repealed.

As amended December 9, 1897.

EXTRACT FROM THE BY-LAWS OF THE CORPORATION.

SECT. VI. — There shall be a Committee on the Society of Arts consisting of five members, appointed at the annual meeting of the Corporation, to hold office for one year, who shall have the general charge and supervision of the organization and proceedings of the Society, subject to the approval of the Corporation. It shall be their duty, in connection with a committee chosen by the Society, to frame By-Laws for the government of the Society, which shall take effect when adopted by the Society and approved by the Corporation.

Revised February 1, 1894.

LIST OF MEMBERS

DECEMBER, 1908

Members are requested to inform the Secretary of any change of address

THE CORPORATION

Life Members

* Blake, Francis	Auburndale, Mass.
* Carson, Howard A.	15 Beacon Street, Boston, Mass.
Choate, Charles F.	50 State Street, Boston, Mass.
Crane, W. Murray	Dalton, Mass.
Draper, Eben S.	Hopedale, Mass.
** Endicott, William	32 Beacon Street, Boston, Mass.
Fairchild, Charles	153 Brattle Street, Cambridge, Mass.
Felton, Samuel M.	528 Dearborn Avenue, Chicago, Ill.
Fish, Frederick P.	84 State Street, Boston, Mass.
* FitzGerald, Desmond	408 Washington Street, Brookline, Mass.
* Freeman, John R.	815 Banigan Building, Providence, R. I.
* Hart, Francis R.	Milton, Mass.
Higginson, Francis L.	274 Beacon Street, Boston, Mass.
Hubbard, Charles W.	133 Essex Street, Boston, Mass.
* Jackson, Charles C.	19 Congress Street, Boston, Mass.
Lee, Elliot Cabot	Brookline, Mass.
Lincoln, William H.	1151 Tremont Building, Boston, Mass.
Livermore, Thomas L.	12 Ashburton Place, Boston, Mass.
* Lowell, A. Lawrence	171 Marlborough Street, Boston, Mass.
* Lowell, Percival	53 State Street, Boston, Mass.
Mills, Hiram F.	266 Andover Street, Lowell, Mass.
* Munroe, James P.	79 Summer Street, Boston, Mass.
Paine, Charles J.	613 Sears Building, Boston, Mass.
Peabody, Robert S.	22 The Fenway, Boston, Mass.
Putnam, William Lowell	60 State Street, Boston, Mass.
* Rotch, A. Lawrence	1124 Board of Trade Building, Boston, Mass.
* Sewall, J. B.	1501 Beacon Street, Brookline, Mass.
Stearns, James P.	National Shawmut Bank, Boston, Mass.
Stockton, Howard	50 State Street, Boston, Mass.

* Stone, Charles A. . . . . 147 Milk Street, Boston, Mass.
Thayer, Nathaniel . . . . 50 State Street, Room 82, Boston, Mass.
* Thomson, Elihu . . . . . 42 Centre Street, West Lynn, Mass.
* Tolman, James P. . . . . 88 Broad Street, Boston, Mass.
Tuttle, Lucius . . . . . 3 North Station, Boston, Mass.
Whitney, David R. . . . . 85 Devonshire Street, Boston, Mass.
* Wigglesworth, George . . . . . 53 State Street, Boston, Mass.
* Williams, Francis H. . . . . 505 Beacon Street, Boston, Mass.

Term Members

Term expires March, 1909

Newell, Frederick H. . U. S. Geological Survey, Washington, D. C.
Stevens, Eben S. . . . . Quinebaug, Conn.

Term expires March, 1910

Copeland, Frederick K. 1506 Railway Exchange Building, Chicago, Ill.
* Gray, Joseph P. . . . . 31 Milk Street, Boston, Mass.
Locke, Frank L., Boston Young Men's Christian Union,
48 Boylston Street, Boston, Mass.

Term expires March, 1911

Du Pont, T. Coleman, E. I. du Pont de Nemours Powder Co.,
Wilmington, Del.
* Main, Charles T. . . . . 45 Milk Street, Boston, Mass.
Wood, Frederick W. . . Maryland Steel Co., Sparrows Point, Md.

Term expires March, 1912

Hale, George E. . . . . Solar Observatory Office, Pasadena, Cal.
Kittredge, George W. . . Grand Central Station, New York, N. Y.
* Stantial, Frank G. . . . Cochrane Chemical Co., Everett, Mass.

Term expires March, 1913

James W. Rollins, Jr. . . . . 922 Beacon Building, Boston
* Everett Morss . . . . . 110 State Street, Boston, Mass.
* A. T. Bradlee . . . . . 78 Chauncy Street, Boston, Mass.

On the part of the Commonwealth

His Excellency the GOVERNOR
The Honorable the CHIEF JUSTICE OF THE SUPREME COURT
The Honorable the SECRETARY OF THE BOARD OF EDUCATION

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* Associate Member, Society of Arts
** Life Member, Society of Arts

LIFE MEMBERS

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Beal, James H. . . . . 104 Beacon Street, Boston, Mass.
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Woodbury, C. J. H. . . . . 45 Milk Street, Boston, Mass.

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Alden, John . . . . . Lawrence, Mass.
Allen, C. Frank . . . Mass. Institute of Technology, Boston, Mass.
Allen, Samuel E. . . . 68 West Worth Street, New York, N. Y.
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THE LABORATORY OF SANITARY CHEMISTRY
XII

THE DETECTION OF FORMIC ACID IN FOODS

BY A. G. WOODMAN AND A. L. BURWELL

WITHIN the last few years several instances have been reported in chemical journals of the use of formic acid as a preservative of foods. There are on the market several preparations sold for food preservation which consist largely of sodium formate. The general interest in the subject led the authors to take up a critical study of the methods for the detection of formic acid.

Most of the tests given in the journals and described in text-books are not suited for use with food materials, in which it is impracticable to separate small amounts of formic acid from other reducing agents. Some of the methods of separation proposed are of value with considerable amounts of formic acid, but not available for the much smaller quantities found in foods. The modification of the ferric chloride test proposed by Smith [1] gives good results in the majority of cases, but the necessity for special precautions in the case of the simultaneous presence of acetates is a disadvantage.

[1] Jour. Amer. Chem. Soc., 29, 1236.

The authors have obtained more generally satisfactory results by means of a method based on the dry distillation of calcium formate. The reaction, as is well known, is

$$\begin{matrix} HCOO \\ \\ HCOO \end{matrix}\!\!\diagdown\!\!\diagup Ca = CaCO_3 + HCHO$$

formaldehyde.

In the presence of any other acid, as, for example, acetic, the reaction is

$$\begin{matrix} HCOO \\ \\ HCOO \end{matrix}\!\!\diagdown\!\!\diagup Ca + \begin{matrix} CH_3COO \\ \\ CH_3COO \end{matrix}\!\!\diagdown\!\!\diagup Ca = 2CaCO_3 = 2CH_3CHO$$

acetaldehyde.

The second reaction was found to give the best results.

The method used may be described briefly as follows: 50 grams of the sample are mixed with 20 c.c. of 20 per cent. phosphoric acid and distilled by steam, the flask containing the acid mixture being gently heated in order to avoid condensation and keep the volume approximately constant. About 200 c.c. should be distilled.

Under these conditions the formic acid is removed practically quantitatively.

To the distillate is added 2 c.c. of 30 per cent. acetic acid, free from formic acid, and 20 c.c. of milk of lime (100 grams CaO per liter). If the distillate should be very acid more lime may be necessary. The solution is evaporated to small bulk over a free flame and then on the water bath to dryness. The evaporation should be carried as far as possible over the flame, because the boiling prevents the formation of the crust of calcium carbonate, which hinders evaporation on the water bath.

The dry residue is scraped into a test tube provided with a cork and a bent delivery tube, and is there subjected to dry distillation. The lower end of the delivery tube, which should be about 60 cm. long, dips into a test tube containing about 3 c.c. of water and immersed in a beaker of cold water. The test tube is heated gradually to redness or until vapors cease to condense in the delivery tube. After the tube has been allowed to drain, 3 c.c. of standard fuchsin-aldehyde reagent is added to the distillate, the mixture allowed to stand exactly five minutes, and compared with a standard color.

The fuchsin-aldehyde reagent is prepared by dissolving 0.2 gram rosaniline in 10 c.c. of freshly prepared *saturated* sulphurous acid, and

allowing the solution to stand until the red color has entirely disappeared, only a light straw tint remaining. The solution is diluted with 200 c.c. of distilled water.

We have found that a slight color is nearly always developed even in the absence of formic acid from the traces of aldehyde produced by decomposing organic matter during the dry distillation. For this reason we have adopted the use of an arbitrary color standard. It is quite possible that the difficulty could be avoided readily also by keeping the temperature of the distillate lower.

The permanent color standard proposed by Jackson[1] for the colorimetric estimation of nitrites was found to be fairly satisfactory as a color standard, although not an exact match in color. To prepare this, 8 c.c. of cupric chloride (12 grams $CuCl_2.2H_2O$ per liter) and 12.5 c.c. of cobaltous chloride (24 grams $CoCl_2.6H_2O$ + 100 c.c. strong HCl per liter) are mixed and diluted to 100 c.c.

By the procedure described a great variety of food products has been tested and found to give a color in no case greater than the standard; the color is usually much less; 0.025 gram of formic acid in 50 grams of the food material gives from four to six times as much color; 0.05 gram gives from ten to fifty times as much.

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[1] TECH. QUART., 13, 314.

DENATURED, OR INDUSTRIAL, ALCOHOL

By RUFUS F. HERRICK

Read January 9, 1908

In addressing the Society on Denatured Alcohol, with special reference to its application in the arts, it has seemed desirable to the lecturer to treat the matter this evening in a very general way. This is partly because of the great scope of the subject, and also on account of the limited time. In order to present the matter in the most comprehensive way the various phases of the manufacture, uses, and possibilities of industrial alcohol will be briefly considered.

The word alcohol is usually understood to mean ethyl alcohol, or ordinary grain alcohol. Alcohol is generally sold of 95 per cent. strength by volume. It is made at the present time on the commercial scale from corn, rye, potatoes, sugar beets, and molasses. The processes used are those of mashing, fermenting, and distilling. Mashing is the process whereby the raw material is prepared for the fermentation.

In the case of corn and potatoes, these materials are mashed by cooking with steam under pressure in order to liquefy the starch present, which is the source of the alcohol. The corn is first ground to meal. In the case of molasses, no grinding or mashing machinery is necessary. In this case the cost of the equipment is correspondingly reduced.

In using sugar beets the juice is extracted by various methods requiring the use of machinery and apparatus. After cooking these raw, starchy materials (corn, potatoes, etc.), the resulting product is properly cooled, and malt is added to transform the starch into fermentable sugar. Yeast is then added for the fermentation of this sugar into alcohol, and is also used in fermenting molasses and the juice of sugar beets. These two latter products contain sugars which furnish the alcohol. Certain precautions in working must be strictly observed to obtain the best possible yields of alcohol.

While it is true that alcohol can be produced from many other raw materials than those just mentioned, more extended investigations and experience are necessary to exactly determine the financial questions which govern in such cases. In Germany potatoes form the chief source of industrial alcohol, while in France sugar beets are solely used, both of these raw materials being grown with special view to produce the largest possible yield of alcohol. In England the conditions governing the raw materials used are somewhat similar to those in the United States. In this country corn has so far been the principal raw material from which industrial alcohol has been made. Molasses is an equally good source for alcohol, and is as readily available for such purposes in this country.

Naturally much interest is felt in the cost of production of alcohol and the future possibilities as to any reduction in such cost in this country. So far it has been difficult to obtain any complete figures, either here or abroad, showing such cost, as it depends upon so many different conditions, including cost of denaturing, and business reasons also prevent such figures being given out. Some credit is obtained for by-products in distilling certain raw materials, but the value of such by-products cannot be readily ascertained.

It may be said, however, that with corn at 52 cents per bushel (the average farm value given by the United States Department of Agriculture for 1907 in this country) a gallon of alcohol of 188° United States proof costs 19½ cents for the corn alone. A United States proof gallon of spirits contains 50 per cent. of absolute alcohol by volume. At this strength it is called 100° proof, or simply "proof" for short.

It is thus seen that 100 per cent. by volume (absolute) alcohol is 200° United States proof, and hence that half the degree proof represents the percentage of absolute alcohol by volume. The 188° proof alcohol mentioned above, therefore, contains 94 per cent. of absolute alcohol by volume.

The average farm value of corn in 1906 was about 40 cents per bushel, according to the United States Department of Agriculture. The yield of alcohol from corn is about 5 gallons of proof spirits from one bushel of corn in modern distilleries operating on the large scale. This is equivalent to 2½ gallons of absolute alcohol. There is some fusel oil produced from distilling corn, and the residue left from the distiliation is of use for feeding cattle. In the case of molasses, about 2¼ gallons of the black strap or low grade molasses left from the

manufacture of sugar is required to produce 1 gallon of 188° proof alcohol. At 7 cents per gallon for this molasses, this represents a cost of about 15¾ cents a gallon for this alcohol, such cost being for the molasses alone.

In Germany 1 gallon of absolute alcohol is obtained from 1¼ bushels of potatoes as an average yield. This is equal to 2 gallons of proof spirits, and it therefore requires 3.12 bushels of such potatoes to equal one bushel of corn in producing alcohol. Compared with corn at 52 cents per bushel, the price paid for such potatoes could only be $\frac{52}{3.12}$, or about $16\frac{8}{10}$ cents per bushel for the making of alcohol. The residue from distilling potatoes is of some value as a food for cattle, and the fusel oil, which can be separated, is also of value.

In the case of production of alcohol in Germany from potatoes, the situation is peculiar to that country. Petroleum products are not native and are taxed, paying a customs duty which substantially helps the industrial alcohol to compete with gasoline and kerosene. In addition, a system exists by which distillers of industrial alcohol benefit from what amounts to a bounty from the government, a portion of the mash-tub tax and distillation tax being rebated. In the report of the British Industrial Alcohol Committee to Parliament, 1905, they say: "The production of spirit in Germany is a state-aided enterprise, . . . and that in the year ended September, 1903, the net subvention of the producers was £2,400,000."

Dr. W. Behrends (a German authority) says: "Taking for granted that 1 hectare of potato land (2.47 acres) produces 150 double cwt. of potatoes, so can at least 16.5 hectoliters (435.7 United States gallons) spirit be manufactured." "This quantity is sufficient to light twelve large street lanterns the entire year for three hours daily on an average, summer and winter. A common-sized village can thus be furnished with good street light from the products of 1 hectare of potato land." "The same quantity is sufficient to operate a 5-horse power spirit motor ten hours daily, Sundays excepted, for three months."

It will thus be seen that in the production of alcohol the choice of the raw material depends upon several factors, chief among which is that of economy. This will depend upon the nature of the soil and on other local conditions.

In addition to the costs for material in making alcohol, there must be added other costs, such as the manufacturing cost, the expense of

the package or barrel, the freight charges, the cost of denaturing, the cost of distribution, and the profits.

The retail price of denatured alcohol in Germany is about one-half that in this country, or about 30 cents per gallon. At present denatured alcohol in the United States is available in only about half the states.

It has been suggested that our farmers now have the opportunity they desired, to see what they can do in making alcohol from their surplus and otherwise waste products. There are about 1,700 small fruit and grain stills in this country, which are used in the season for making brandy and whisky. Can these be employed for the manufacture of alcohol? A proper investigation would show farmers what the possibilities are for making alcohol by coöperative effort and with distilleries managed for them by practical distillers, assisted by experienced chemists. The farmers have been successful in the making of butter, the management of dairies, etc., along coöperative lines. That the best results with alcohol may be expected from a similar plan of action is suggested by United States Consul General R. P. Skinner, who says, as a result of his investigation in France concerning farmers' stills, that "in the United States the farmer can proceed under no illusion that first-class crops can be converted into alcohol in small domestic stills on a profitable basis." The French statistics given by Consul General Skinner (1907) refer to alcohol made by farmers for consumption.

Denatured alcohol is simply ordinary alcohol to which some foreign substance has been added. It is thus rendered repugnant in taste and odor and injurious to health and eyesight. After this is done the alcohol is deprived of its nature (denatured) as a beverage and cannot be used for drinking purposes. Any attempted purification of it is impracticable on account of the difficulty and cost. Indeed, the history of the many countries permitting the use of denatured alcohol shows that no appreciable amounts of fraud upon the revenue has resulted therefrom, and none of these countries have ever repealed such beneficent legislation. In fact, the last report of the United States Commissioner of Internal Revenue says, "It is a subject of congratulation that few if any frauds have been committed or attempted in connection with the manufacture or use of this class of spirits."

The object of denaturing alcohol is to avoid the excise or spirit tax. It thus becomes greatly cheapened in price, as this tax on ordinary alcohol amounts to about $2.08 per gallon.

The denaturing of the alcohol does not injure its properties for industrial uses in any way. The list of substances used for denaturing, or, as it is called in England, "methylating," is very large. The word methylating was used because wood alcohol, the first substance so used in England, consists largely of methyl alcohol. Wood alcohol was first used for such purpose in England in the year 1855.

In the United States the law permitting denatured alcohol went into effect January 1, 1907. This law was subsequently greatly liberalized by amendments which were enacted and which went into effect September 1, 1907.

There are two kinds of denatured alcohol; one is called completely denatured, the other specially denatured. Two formulas are permitted by our government for completely denaturing alcohol for general uses of light, heat, and power, and for manufacturing purposes.

1. To 100 gallons of ethyl alcohol not less than 180° proof add
   10 gallons of approved wood alcohol,
   ½ gallon of approved petroleum benzine.
2. To 100 gallons of ethyl alcohol not less than 180° proof add
   2 gallons of approved wood alcohol,
   ½ gallon of approved pyridine bases.

The first of these formulas is the one that has been used.

As completely denatured alcohol cannot be used in many industries, the government permits special denaturing agents to be used in such cases. Among such special denaturing substances may be mentioned wood alcohol, camphor, benzol, castor oil and soda lye, nicotine, sulphuric or common ether, pyridine bases, acetone, petroleum naphtha, etc.

Included in the large number of industries benefiting from the use of denatured alcohol are those making furniture, pianos, trolley and steam cars, perambulators, toys, caskets, wood finishing and decorating, watches, photographic supplies, chemical manufactures, dyes, collodion, whips, varnishes and lacquers from soluble cotton, imitation leather, artificial silk, photo-engravings, purification of rubber, shellac and spirit varnishes, electrical industries, celluloid, smokeless powder, common ether, ethyl chloride, etc.

Many other industries will doubtless be added to these as time passes, because the use of specially denatured alcohol is bound to be largely extended. In France and Germany the special denaturing is much more satisfactorily done at the factory or works where the alcohol is used. The quantity of denatured alcohol used annually in Germany is

something like 37,000,000 gallons, in France about 10,000,000 gallons, and in England about 4,000,000 gallons. Of the above, about 2,000,000 gallons of specially denatured alcohol are used in France, and about 7,000,000 gallons of specially denatured alcohol are used in Germany.

In this country during the past year there have been used about 3,500,000 gallons of denatured alcohol, of which a large part was specially denatured.

Lack of alcohol-using appliances and apparatus, lack of suitable special denaturing formulas at the beginning, the great reduction in the price of wood alcohol, and the high retail price of denatured alcohol have prevented the large immediate use that many believed would result.

England has recently permitted a reduction of from 10 to 5 per cent. in the amount of wood alcohol used for denaturing, and omits the light mineral oil. This formula is used for general industrial purposes, and should largely increase the use of denatured alcohol in England.

The latest available figures show the wholesale cost of denatured alcohol in England to be about 42 cents per gallon. In France the retail price (August 6, 1906) was about 44 cents per United States gallon.

In Cuba the cost by the large package, 173 United States gallons of denatured alcohol, is about 28½ cents per gallon. The retail price in bottles, about the fifth of a gallon in capacity, is 8 cents.

Among notable instances of the uses of specially denatured alcohol are the samples, here shown, of artificial silk made in France from cotton by the Chardonnet process. About 3,800 gallons of alcohol are used daily in the factory at Besançon, France, where about 2,640 pounds per day is made of this silk. About 1.43 gallons of alcohol are required for each pound of silk. Methyl alcohol has proved unsuitable. The French government permits the ether required to be used as the denaturing agent. In the above amount of alcohol is included the quantity necessary to be made into ether for the solvent, a mixture of alcohol and ether being used for this purpose. The samples of artificial silk exhibited include all colors and many handsome woven brocade effects, braids, bindings, and hanks, as well as artificial horsehair, also made in the same way from cotton. All these samples were imported.

Imitation leather, of which samples are shown, is largely used in making automobile tops, carriages, upholstering, etc. It consists of

a backing of heavy cotton cloth, on which an insoluble flexible preparation is applied by machinery. It may be made in various colors, and the freedom from odor, the flexibility, and fine appearance of the samples will be seen. Such leather is made abroad as well as in this country, the samples shown being of domestic manufacture. Specially denatured alcohol is used as a solvent in making such imitation leather.

A series of lantern slides[1] will now be shown, illustrating the principles and operation of the machinery and apparatus used in manufacturing alcohol, and also showing the great variety of alcohol-using appliances, illuminating lamps, blue-flame cooking and heating alcohol stoves, alcohol-heating flatirons, alcohol-using motors, etc.

For illumination, one-half gallon of alcohol is about equal to 1 gallon of kerosene. The alcohol lamp is under perfect control, is cleanly, and does not burn a wick. As a source of power, German spirit-motor tests show[2] that "although the amount of heat produced from spirit is considerably dearer than if obtained from gasoline or kerosene, yet in consequence of the technical heating superiority of the spirit motor the amount of work of one effective horse power is almost the same in all these fuels." The principles of several mechanical distributing carburetors are shown by these lantern slides, and attention should be directed to the importance of complete vaporization of the alcohol and increased compression necessary in using spirit motors. The alcohol illuminating lamps shown include the best French and German models, using in all cases a Welsbach mantle, which is rendered incandescent by the burning mixture of alcohol vapor and air. This mixture is made automatically by the vaporizer in these lamps. Most of the specimens of the alcohol apparatus and alcohol appliances shown are imported, and the prices are increased in this country on account of customs, duties amounting in some cases to about 45 per cent. There will therefore be a decrease in the prices of such appliances when our manufacturers make them in this country.

The cost of common ether has been greatly reduced in consequence of the denatured alcohol law, and the same can be said of collodion. These are very important products. Reductions in prices of other

[1] From illustrations in Mr. Herrick's book, Denatured, or Industrial, Alcohol. New York: John Wiley & Sons.

[2] From review by K. Fehrmann of spirit-motor tests made by Prof. E. Meyer, in May, 1902.

products for which alcohol is used may also be expected in a number of cases.

Alcohol is an ideal fuel, burning completely with formation of carbon dioxide and water (as vapor). It fouls the atmosphere very much less than gasoline, kerosene, gas, or acetylene. It mixes with water, and a fire once started is therefore readily extinguished; while fires from gasoline and kerosene, on the contrary, are merely further spread by the action of water. From the insurance point of view of fire risk denatured alcohol may be regarded as about the same as ordinary alcohol, being less hazardous than wood alcohol in such respects.

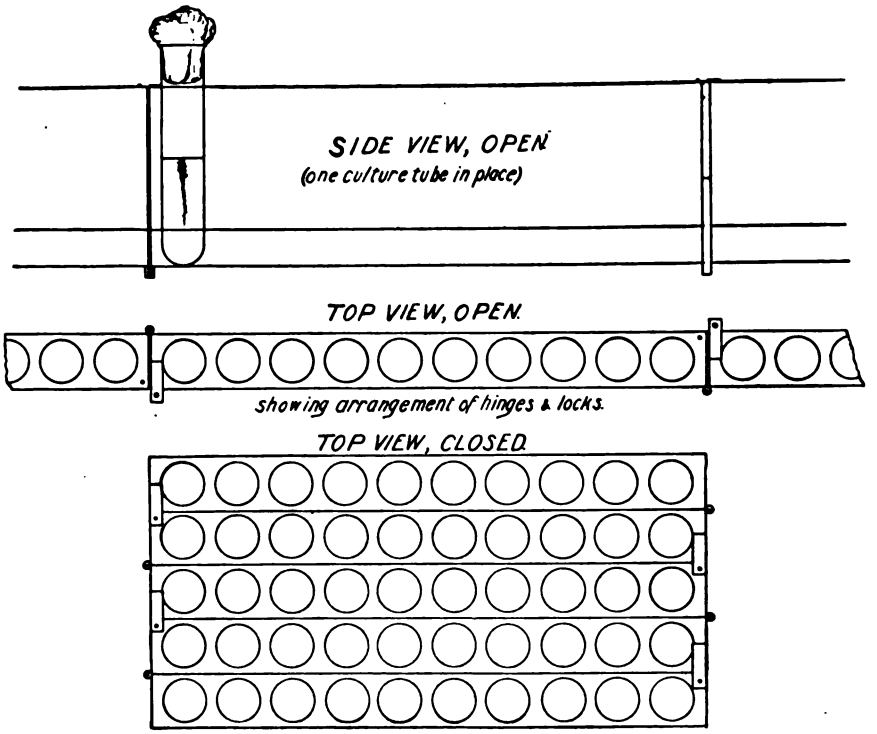
Eminent authorities have pointed out the possibilities of cellulose and other sources for producing industrial alcohol, and many patents are being taken out for continuous methods of distilling alcohol, the synthetic manufacture of alcohol from acetylene derived from calcium carbide, the enrichment of alcohol vapors with acetylene, etc. The investigation of cheaper sources of starch than corn for making alcohol is under way, and the excellent possibility of low-priced alcohol when it may be made in Porto Rico and the Hawaiian Islands from residual low grade molasses remains to be investigated and worked out.

CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES

A CULTURE-TUBE RACK FOR USE IN BACTERIOLOGICAL STUDIES INVOLVING A LARGE NUMBER OF CULTURES

BY LAURENCE T. WALKER

IN carrying on bacteriological investigations or routine work in which a large number of cultures are incubated under identical conditions, and studied simultaneously, there is a great loss of time and an appreciable danger of error due to the difficulty of handling the culture-tube racks commonly in use. For study, the most convenient arrangement of cultures is in a single line on the laboratory bench; in the



CULTURE-TUBE RACK FOR USE IN BACTERIOLOGICAL STUDIES

incubator, where economy of space must be considered, it is necessary to mass in rows, placed side by side. Thus the single-line racks are excellent for use while examining cultures, and the square or oblong holders containing a large number of tubes are most suitable for incubating. Either the work must be done under adverse conditions or the cultures must all be transferred from one holder to another each time they are examined — a process involving extra labor and possible contamination in a daily or even weekly examination of a series of a hundred or more tubes.

The holder suggested is one in which a large number of tubes (fifty in the model) are compactly massed for incubation, and in which they may be arranged in single line for examination without removal. It is in effect a number of single-line racks so connected, end to end, by hinges that the whole may be closed like a folding screen or opened so as to display fifty tubes in a row. When closed the whole is held firm by small spring catches attached to the different sections. The model shown in the figure is constructed of sheet metal, thus fulfilling the requirements of lightness, cleanliness, and durability necessary in an apparatus of this nature.

CONTRIBUTIONS FROM
THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
No. 23

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS[1]

PART III. ANALYSIS OF THE ALUMINUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM

BY ARTHUR A. NOYES, WILLIAM C. BRAY, AND ELLWOOD B. SPEAR

INTRODUCTION

THIS article is a continuation of a preceding one which appeared in an earlier number of this QUARTERLY, in which were presented the first two parts of this "System of Qualitative Analysis," dealing with the "Preparation of the Solution," and the "Analysis of the Silver, Copper, and Tin Groups."[2] For the purposes of this investigation, for the general considerations underlying it, and for various conventional matters relating to its presentation, the reader is referred to the Introduction to the preceding paper.

Although the final form of the scheme of analysis of the groups here considered has been worked out during the past year by the authors of this article, yet much of the preliminary experimental work, especially that relating to the rarer metals included, was carried on by others in this laboratory. It is unfortunately scarcely practicable to indicate in just what respects each of these investigators has contributed to the final result; but we wish to express in a general way our great indebtedness to Messrs. Howard I. Wood, Barthold E. Schlesinger, and Charles Field 3rd, for the assistance which their work has been to us.

The present publication deals with the analysis of the precipitate produced by ammonium hydroxide and sulphide in the filtrate from the hydrogen sulphide precipitate. In addition to the seven common

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[1] Copyright, 1908, by ARTHUR A. NOYES.

[2] This QUARTERLY, 19, 191 (1906).

elements (nickel, cobalt, iron, manganese, zinc, chromium, and aluminum) considered in almost all schemes of qualitative analysis, we have included six of the especially important rarer elements, namely, beryllium, uranium, vanadium, thallium, titanium, and zirconium. The portions of the procedure and of the notes referring to these rarer elements are, however, marked with asterisks, so that they may readily be omitted by any one interested only in the common elements.

The general features of our scheme for the analysis of this solution will be most readily comprehended by an examination of the "Tabular Outline" presented in Tables VII to IX. The considerations which have led to the adoption of this procedure will be discussed in the next chapter, entitled "General Discussion," and the detailed process and the explanations of it will be presented in the following one, entitled "Procedures and Notes." Later chapters, as in the preceding publication, will be devoted to the "Test Analyses" and to "Confirmatory Experiments and References."

General Discussion

1. With respect to the original precipitation of these elements, schemes of qualitative analysis differ as to whether ammonium hydroxide and ammonium sulphide be used successively with a filtration between, or whether they be added together so that all the elements are contained in a single precipitate. The former of these methods has the serious disadvantage that the separation with ammonium hydroxide of the trivalent elements, aluminum, chromium, and ferric iron, from the bivalent elements, nickel, cobalt, manganese, and zinc, while satisfactory enough when certain combinations of these elements are present, is not so for other combinations. Thus even a large quantity of zinc may be quantitatively precipitated by ammonium hydroxide when a larger proportion of chromium is present; and manganese will in any case be partially precipitated by that reagent, owing to its oxidation by the air to the manganic state, and it will be completely precipitated when phosphate is present in the solution. It is therefore necessary to provide for the detection of zinc and manganese both in the hydroxide and in the sulphide precipitate; and thus the scheme is complicated rather than simplified by precipitating separately with these reagents.

We have, therefore, adopted the plan of a single precipitation by simultaneous addition of both reagents, provision being made, however,

for observing the effect of the addition of ammonium hydroxide alone for the sake of the indications which it may furnish. If care be taken to avoid an unnecessary excess of both the hydroxide and sulphide, all the elements in question are completely precipitated by these reagents even in moderately dilute solution, with the exception of a little of the nickel and a variable proportion of the vanadium. The nickel can be removed from the filtrate by boiling. Even a large quantity of vanadium remains completely in solution when it is present alone; but on the other hand, it may be almost completely precipitated, probably as a hypovanadate or vanadate, when certain other elements of these groups are present. Many experiments were made in this laboratory by Mr. Charles Field 3rd, to devise a practical method of reducing vanadium to a vanadic salt (corresponding to the oxide V_2O_3), in which state it is completely precipitated by ammonium hydroxide. In accordance with the results of Gooch and Curtis[1] hydriodic acid (best in the form of a mixture of ammonium iodide and hydrochloric acid) was found to be the only available agent, but even with the aid of this reagent reduction and precipitation were never quite complete and sometimes did not take place at all. For this reason it was not considered worth while to use this reagent, especially since the vanadium can be removed from the ammonium sulphide filtrate by acidifying, adding ferric chloride, and making alkaline with ammonia.

2. The ammonium sulphide precipitate in all the schemes of analysis known to us is first treated with cold, dilute hydrochloric acid, in order to separate nickel and cobalt from the other elements. In spite of the general use of this process, we have become convinced that it does not fulfil the requirements of exact qualitative analysis; for not only is it true, as is generally known, that a considerable quantity of nickel and cobalt dissolves in a mixture of 1 volume of HCl (1.12) with 5 volumes of water when there is a large residue containing these elements, but our experiments have shown that a moderate quantity of either of them (up to at least 5 mgm.) may *completely* dissolve, and thus escape detection, when it was originally disseminated through a large precipitate of iron sulphide. We have therefore eliminated this treatment as a method of separation; and, after adding hydrochloric acid at first to decompose such of the sulphides as it will act upon and to get an indication as to the presence of much nickel or cobalt, nitric acid is

[1] Am. J. Sci. (4) 17, 45 (1904).

added, so as to bring all the elements into a single solution. Incidentally it may be mentioned that our experiments support the view that the fact that nickel and cobalt sulphides, though not precipitated by hydrogen sulphide from a slightly acid solution, yet dissolve difficultly in a much stronger acid, is due to an abnormally slow rate of solution of these sulphides, which are, in fact, relatively soluble substances, at least in the freshly precipitated state. For these experiments have shown that nearly all of a portion of precipitated nickel sulphide dissolves when treated with successive portions of cold dilute HCl [1 volume HCl (1.12) with 5 volumes of water] even when the acid is kept saturated with hydrogen sulphide, and that solution continues to take place even after considerable nickel (30 mgm. in 30 ccm.) has passed into solution. When, therefore, the surface exposed to the acid is greatly increased, either by the residue being a large one or by a small residue being left in a finely divided state by the dissolving out of iron sulphide, a considerable quantity of nickel and cobalt passes into solution in a comparatively short time. It is interesting to note that the reverse reaction, the precipitation of nickel sulphide by hydrogen sulphide in acid solution, also takes place very slowly; for Baubigny[1] has observed that in the presence of acetic acid, or of very small amounts of sulphuric or hydrochloric acids, the precipitation is a slow but continuous process.

3. Having now all the elements together in solution, the next step in our process is to divide them into two main groups by the addition of sodium hydroxide and peroxide, followed by subsequent boiling. This method has been previously applied by other authors to the separation of certain of the common elements, but not, we believe, as a general means of subdivision. These reagents cause the complete precipitation of iron, nickel, cobalt, and thallium as hydroxides of the trivalent form, and of manganese, titanium, and zirconium as hydroxides of the quadrivalent form. We shall designate all these elements so precipitated as the "iron group." All the remaining elements, namely, aluminum, beryllium, zinc, chromium, uranium, and vanadium, remain in solution in the form of sodium salts of the corresponding acids, namely, as aluminate, zincate, chromate, peruranate, and vandate. We shall designate all these elements so dissolved as the "aluminum group." The separation of the two groups by this process is entirely satisfactory,

[1] Baubigny, Compt. rend., 94, 963, 1183, 1251, 1417, 1473, and 1715 (1882), and 95, 35 (1882).

at any rate from the standpoint of qualitative analysis, with the single exception that when only 5 or 10 mgm. of zinc are present, this may be carried down completely when elements of the iron group (especially manganese) are present in large quantity. This makes it necessary to provide for the detection of zinc in the analysis of the precipitate when it is large, but this is not attended with special difficulty. The use of sodium peroxide has the distinct advantage over that of sodium hydroxide alone, that chromium, uranium, and vanadium are by the use of the peroxide taken completely into solution, whereby not only a division of these elements between the precipitate and filtrate is avoided, but also the carrying down of zinc into the precipitate is made less common and less considerable.

4. Since, owing to the possible presence of phosphate, oxalate, or hypovanadate in the original solution, the alkaline-earth elements may be precipitated by ammonium hydroxide and sulphide, sodium carbonate is added with the hydroxide and peroxide, in order to ensure the complete precipitation of these elements (more especially barium) with the iron group. The presence of phosphate and carbonate does not affect at all the separation of the elements of the aluminum and iron groups from each other.

5. The separation of the elements of the aluminum group from each other is very simple when only the common elements, chromium, aluminum, and zinc, are to be provided for; and the process recommended below for this case offers no original features. It consists in precipitating the aluminum hydroxide from the solution with ammonium hydroxide after acidifying with nitric acid, the chromate in the filtrate with barium chloride after acidifying with acetic acid, and the zinc with hydrogen sulphide in the filtrate from the barium chromate.

6. The presence of beryllium does not involve any complication, since it goes with the aluminum in the process just referred to, and can be separated from it as described below. When, however, uranium and vanadium are to be provided for, this process is entirely inadequate; for upon the addition of ammonium hydroxide after acidifying, vanadium divides between the filtrate and precipitate wherever uranium is present, owing to the insolubility of uranyl vanadate; uranium itself will divide, owing to the presence of H_2O_2 formed on acidifying the sodium peruranate solution; and vanadium, when present in large amount, again divides upon the addition of barium chloride to the acetic acid solution, owing to the slight solubility of barium vanadate; finally,

vanadium interferes with the test for zinc with H_2S in acetic acid solution, since a precipitate of sulphur is always formed and sometimes one of black vanadium sulphide. Moreover, the uranium precipitate obtained with ammonium hydroxide will in general be mixed with aluminum, beryllium, and vanadium, so that the difficult part of the separation still remains to be accomplished. After much experimenting, guided by the conception that under proper conditions of alkalinity it might be possible to separate the more basic elements, zinc, aluminum, and beryllium, from those present as constituents of acid radicals, chromium, uranium, and vanadium, it was finally found that this could be accomplished in a hot dilute solution of sodium hydrogen carbonate, provided care be taken to prevent loss of carbon dioxide by heating the solution in an open vessel only to 90°, or better in a closed bottle to 100°. Under these conditions the separation is a fairly satisfactory one. A small amount of uranium may, however, be carried down almost completely when a large amount of aluminum or beryllium is present, making it necessary to test for uranium in the precipitate. Moreover, when uranium and vanadium are simultaneously present, each in large quantity (about 100 mgm.), some uranyl vanadate precipitates, but a large quantity of both elements remains in the solution, so that their detection is not interfered with.

7. The separation of the zinc from the aluminum and beryllium in the precipitate is readily effected by dissolving it in hydrochloric acid and adding a small excess of ammonium hydroxide. For the separation of the aluminum and beryllium from each other we studied what seemed to be the two most promising methods mentioned in the literature. The first of these was that described by Parsons and Barnes,[1] which consists in boiling for a short time a solution of the two elements to which enough sodium hydrogen carbonate is added to make a 10% solution, whereby aluminum is precipitated and beryllium dissolved. We found, however, that though this method is satisfactory for the detection of beryllium when a moderate amount of aluminum is present, yet with a large quantity of aluminum (say, 100–500 mgm.) 2–5 mgm. of beryllium are almost completely retained in the precipitate, which may cause it to escape detection, and which at any rate leads to an incorrect estimate of its quantity. The second method investigated was that proposed by Havens,[2] which consists in saturat-

[1] J. Am. Chem. Soc., 28, 1589 (1906).

[2] Z. anorg. Chem., 16, 15 (1898).

ing a solution of the chlorides of the two elements in a mixture of ether and strong hydrochloric acid with hydrogen chloride gas, whereby aluminum is precipitated and beryllium remains in solution. It was found that this method gives entirely satisfactory results, even 0.5 mgm. of aluminum being precipitated, as $AlCl_3.6H_2O$, provided care be taken to use a sufficient proportion of ether and to saturate completely with the gas; moreover, even 100 mgm. of beryllium remain wholly in solution and even 0.5 mgm. is not carried out with a large quantity of aluminum. This method was, therefore, adopted for the separation, it being supplemented by a confirmatory test for beryllium based on the process of Parsons and Barnes.

8. The separation of the chromium, vanadium, and uranium, which are present together in the filtrate from the sodium hydrogen carbonate precipitate, also required much investigation. It was soon decided that there was more promise of effecting a separation of the first two of these elements in the state of chromate and vanadate, in which they already exist, than in a lower stage of oxidation; and it was found that the lead salts differed sufficiently in solubility in nitric acid to enable 0.5 mgm. of chromium to precipitate while retaining 100 mgm. of vanadium in solution. A separation based on this fact was therefore adopted. The excess of lead added is subsequently removed by saturating the filtrate with hydrogen sulphide. To avoid the addition and removal of lead when chromium is absent, a preliminary test for chromate with hydrogen peroxide is introduced. The uranium is separated from the vanadium (after oxidation to the vanadic state) by precipitating it as uranyl ammonium phosphate in acetic acid solution,—a method that was found to give satisfactory results for the limiting case of a large proportion of uranium and a small proportion of vanadium, and also in the converse case. Vanadium is tested for by making the filtrate strongly alkaline with ammonia and saturating with hydrogen sulphide, whereby a violet red solution of a vanadium sulpho-vanadate is formed.

9. We will next consider the analysis of the precipitate produced by sodium peroxide and containing the manganese, iron, nickel, cobalt, thallium, titanium, and zirconium, and the alkaline-earth elements. The main problems connected with this were the separation of the manganese from the other elements, that of the alkaline-earth elements from phosphate, and that of the titanium and zirconium from the iron and from each other.

10. In almost all schemes of qualitative analysis it is thought

sufficient to test a portion of the precipitate for manganese by fusing it with sodium carbonate or by boiling it with lead dioxide and nitric acid, without isolating the manganese. These color tests give, however, but little idea of the quantity of the element present. Moreover, aside from this objection, the large number of the elements contained in the precipitate in this scheme makes their separation necessary. The one reaction of manganese which seemed in every way suited for this purpose is that frequently employed in iron and steel analysis, consisting in the conversion of the manganese into the dioxide by the action of chloric acid and concentrated nitric acid. For this is not only a behavior highly characteristic of this element, but since the separation is carried out in a strongly acid solution it might be anticipated that the other elements, which are not oxidizable to insoluble peroxides, would not be retained in the precipitate to an important extent. Our experiments have shown that this is in general the case, but one exception has been discovered. It has been found, namely, that titanium, which is quadrivalent like manganese in the dioxide, when present even in considerable quantity (up to 50 mgm.) may be completely precipitated with a large quantity of manganese (500 mgm.), and that a large proportion, though not all, of the zirconium is likewise carried down. The method is, however, otherwise so satisfactory that we have adopted it, special provision being made for this unusual case in a way that need not be described here. The procedure consists in dissolving the whole sodium peroxide precipitate in strong hydrochloric acid, in evaporating with excess of nitric acid, adding concentrated nitric acid and potassium chlorate, heating, and filtering off the manganese dioxide on an asbestos filter.

11. Owing to the fact mentioned above that zinc is carried down in considerable quantity by manganese in the Na_2O_2 precipitation, experiments were made with the view of previously removing manganese by introducing this chloric acid procedure at the beginning of the analysis of this group. It was found, however, that vanadium, which is not carried down in the sodium peroxide procedure, is, like titanium, precipitated in large quantity with the manganese in the chloric acid procedure. It was found also that some zinc (1–4 mgm.) may be carried down completely in the Na_2O_2 precipitate by iron, nickel, and cobalt, so that it would be still necessary to provide for the detection of zinc in the iron group. For these reasons it is evidently best to have the sodium peroxide precipitation precede the treatment with chloric acid.

12. The filtrate from the chloric acid precipitate is first tested for phosphate. When it is not present, the iron, thallium, titanium, and zirconium are separated from the other elements by the addition of ammonium hydroxide. When phosphate is present, in order to separate it from the alkaline-earth elements, the basic acetate precipitation is employed, ferric chloride being first added if necessary. The provision here made for the case that phosphate is present is thought to have many advantages over the methods ordinarily employed in schemes of qualitative analysis, where the phosphate is removed by tin in nitric acid solution, by ferric chloride and barium carbonate, or by ferric chloride and ammonium acetate in the first stages of the analysis of the group. Of these three processes, the basic acetate is much more rapid and simple of execution, but it does not give a separation which is at all satisfactory when applied to a solution containing all the elements of the aluminum and iron groups; thus chromium and zinc may in certain combinations of elements be found either in the precipitate or filtrate, and manganese also divides unless great care is taken to make the precipitation in a large volume at the proper acid concentration. In the scheme of analysis here presented this basic acetate separation has been introduced only after these troublesome elements have already been removed, for the presence of phosphate involves no complications in the preceding steps of the process. Under these circumstances it is no more difficult to secure accurate results in this separation than in the precipitation with ammonium hydroxide. Indeed, by adopting this process for all cases the complication of the alternative procedure and the special test for phosphate might be removed; but since the operations require a somewhat longer time, it has seemed best to retain the ammonium hydroxide precipitation for the case that phosphate is not present.

13. The iron might be separated from the titanium and zirconium by the well-known method of boiling a solution of the elements kept slightly acid with sulphurous acid; but it is difficult to secure complete precipitation of the titanium and zirconium, and at the same time to prevent the carrying down of iron. Besides this the operation is a long one, involves large dilution, and makes it necessary to use hydrofluoric acid in redissolving the precipitated hydroxides. On the other hand, the removal of the iron by the method of Rothe,[1] which consists in shaking it out of a strong hydrochloric acid solution by means of

[1] Stahl und Eisen, 12, 1052 (1892); 13, 333 (1893).

ether, is extremely simple and rapid, gives a perfect separation, and leaves the titanium and zirconium in solution. We have, therefore, unhesitatingly employed this method in our scheme of analysis. Moreover, in this process the thallium, which is present as thallic chloride, is extracted, together with the ferric chloride, by the ether; and it can be readily detected after evaporating off the ether and reducing the ferric and thallic salts with sulphurous acid by the formation with potassium iodide of the characteristic yellow precipitate of thallous iodide.

14. For the separation of the titanium and zirconium from each other we have adopted the process of Hillebrand,[1] which consists in adding sodium phosphate to a slightly acid solution containing hydrogen peroxide, whereby the zirconium is precipitated and the titanium remains in solution. The latter is shown to be present by the color of the solution, but it can also be precipitated as phosphate by destroying the hydrogen peroxide with sulphurous acid after filtering off the zirconium compound.

15. The analysis of the ammoniacal solution containing nickel, cobalt, and perhaps zinc and the alkaline-earth elements, is carried out along the conventional lines. The first three elements are precipitated by the addition of ammonium sulphide, and the zinc is extracted, if the precipitate is large by treating it with cold, dilute hydrochloric acid, or if it is small by dissolving the precipitate completely and treating again with sodium peroxide. Instead of separating the nickel and cobalt from each other, it was found to be shorter and more conclusive to divide the solution of the sulphides into two parts, and to test one portion for nickel by adding potassium cyanide and sodium hypobromite, and the other portion for cobalt with potassium nitrite. The conditions for securing the best results in the nickel test were fully studied. Finally, in the filtrate from the ammonium sulphide precipitate the alkaline-earth elements are precipitated with ammonium carbonate as usual.

16. Though no provision is made in the system of analysis for the separate detection of any of the rare-earth elements, yet a process has been described for determining whether any of them are present and for removing them when they are found to be in the solution. This process consists in evaporating the acid solution of the original

[1] Bull. U. S. Geol. Survey, No. 176, p. 75 (1900).

ammonium sulphide precipitate, adding to the residue hydrofluoric acid, and filtering. This converts the rare-earth elements completely into insoluble fluorides, and enables them to be separated from all the other elements of the aluminum and iron groups (except from a very large quantity of aluminum). When alkaline-earth elements are present these are also precipitated as fluorides, wholly or in part, and are separated from the rare-earth elements by decomposing the fluorides with sulphuric acid, diluting, filtering off any alkaline-earth sulphates that separate, and precipitating the rare earths in the filtrate with ammonium hydroxide. This process of isolating the rare-earth elements has been worked out in this laboratory by W. C. Arsem and H. I. Wood for use as a group separation in the "System of Qualitative Analysis Including Nearly All the Metallic Elements."[1]

17. Final confirmatory tests are given for almost all the elements, and much experimenting has been done on some of these tests in order to make them delicate and reliable; thus this is true of the color tests for aluminum and zinc made by igniting the oxides with cobalt nitrate, of that for chromium with hydrogen peroxide and ether, of that for nickel with H_2S in an alkaline tartrate solution, and of that for vanadium made by adding H_2O_2 to an acid solution; also of the precipitation test for uranium with potassium ferrocyanide. No satisfactory tests have as yet been found for beryllium or zirconium. Many, but not all, of these confirmatory tests will be found superfluous and will be omitted by the experienced analyst, except in cases where a very small precipitate or one of doubtful character is obtained; but they will, we believe, be useful to those unfamiliar with this scheme, and they serve in the case of students the educational purpose of making them acquainted with additional reactions of the elements in question.

18. It may be thought an objection to this scheme of analysis that it involves a number of manipulative operations unusual in qualitative analysis, such as heating in a closed bottle, saturating the acid-ether solution with hydrogen chloride gas (in the separation of aluminum and beryllium), filtering through an asbestos filter (in the separation of manganese), and shaking out with ether in the separation of iron from titanium and zirconium. These operations, when they have been once executed, are found to be little, if any, more troublesome than the ordinary operations of precipitation and filtration. They are, moreover,

[1] Two parts of this "System" have already been published. See TECH. QUART., 16, 93-131 (1903); 17, 214-257 (1904).

mostly employed only in connection with the detection of the rarer elements, where the difficulties in finding any satisfactory method are so great that a little additional trouble is an insignificant factor. And finally, from an educational standpoint, they introduce the student to new kinds of processes, thus enlarging his knowledge and diminishing the force of the objection that the ordinary study of qualitative analysis is too limited in its scope.

Tabular Outline

In the tables below the enclosure of a symbol in brackets shows that the element may divide itself between the residue and the solution in the operation immediately preceding.

TABLE VII

ANALYSIS OF THE ALUMINUM AND IRON GROUPS FOR COMMON ELEMENTS

To the filtrate from the H_2S precipitate add NH_4OH and $(NH_4)_2S$ (P. 51).

Precipitate $Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, Fe_2S_3, NiS, CoS.
Dissolve in HCl or HCl + HNO_3, evaporate, add NaOH, Na_2O_2, and Na_2CO_3 (P. 52).

Filtrate: alkaline earth and alkali elements.

Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2.
Acidify with HNO_3, add NH_4OH (P. 53).

Precipitate: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$ [ZnO_2H_2].
Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).

Precipitate: $Al(OH)_3$.
Dissolve in HNO_3, add $Co(NO_3)_2$, evaporate, ignite (P. 54).

Blue residue: $Al_2O_3.xCoO$.

Filtrate. *Add $HC_2H_3O_2$ and $BaCl_2$ (P. 55).*

Precipitate: $BaCrO_4$.
Dissolve in dilute HNO_3, add ether and H_2O_2 (P. 56).

Blue coloration of ether layer: H_3CrO_7.

Filtrate: Zinc salt.
Pass in H_2S (P. 57).

White precipitate: ZnS.
Dissolve in HNO_3, add $Co(NO_3)_2$ and Na_2CO_3, ignite (P. 57).

Green residue: $ZnO.xCoO$.

Precipitate: MnO_2.
Boil with HNO_3 and PbO_2 (P. 62).

Violet color: $HMnO_4$.

Solution.[1] *Add NH_4OH (P. 64).*

Precipitate: $Fe(OH)_3$.
Dissolve in HCl, add KSCN.

Red solution: $Fe(SCN)_3$.

Filtrate: $Co(NH_3)_x(NO_3)_2$, $Ni(NH_3)_4(NO_3)_2$, $Zn(NH_3)_4(NO_3)_2$. *Pass in H_2S (P. 66).*

Precipitate: ZnS, CoS, NiS.
Treat with cold dilute HCl (P. 67).

Solution: $ZnCl_2$, [$CoCl_2$], [$NiCl_2$]. *Add NaOH and Na_2O_2 (P. 67).*

Residue: NiS, CoS

Solution: Na_2ZnO_2.
Add $HC_2H_3O_2$ and H_2S (P. 57).

White precipitate: ZnS.

Precipitate: $Co(OH)_3$, $Ni(OH)_{2-3}$.
Dissolve, evaporate, add NaOH.

To one half add KNO_2 and $HC_2H_3O_2$ (P. 69).

Yellow precipitate: $K_3Co(NO_2)_6$.

To other half add KCN, digest, add NaBrO (P. 70).

Black precipitate: $Ni(OH)_3$.

[1] Test for phosphate at this point (P. 63); if present follow Table IX.

TABLE VIII

Analysis of the Aluminum Group for Common and Rare Elements

Filtrate from Na_2O_2 treatment: Na_2CrO_4, sodium peruranate, Na_3VO_4, Na_2ZnO_2, $NaAlO_2$, Na_2BeO_2.
Add HNO_3, dilute, add $NaHCO_3$, heat in a closed bottle (*P. 58a).

<table>
<tr><td colspan="4">Filtrate: Salts of chromic, uranic, and vanadic acids. Add HNO_3 and $Pb(NO_3)_2$ (*P. 58b).</td><td colspan="4">Precipitate: $ZnCO_3$, $Al(OH)_3$, basic $BeCO_3$. Dissolve in HCl, add NH_4OH (*P. 58f).</td></tr>
<tr><td rowspan="4">Yellow precipitate: $PbCrO_4$.</td><td colspan="3">Filtrate: $UO_2(NO_3)_2$, H_3VO_4, $[Pb(NO_3)_2]$. Pass in H_2S.</td><td rowspan="2">Filtrate: $Zn(NH_3)_4Cl_2$. Add $HC_2H_3O_2$, pass in H_2S (P. 57).
White precipitate: ZnS.</td><td colspan="3">Precipitate: $Al(OH)_3$, $Be(OH)_2$. Dissolve in HCl, add ether, saturate with HCl gas (*P. 58g).</td></tr>
<tr><td rowspan="3">Precipitate: PbS. Reject.</td><td colspan="2">Filtrate. Add bromine, neutralize, add $HC_2H_3O_2$ and Na_2HPO_4 (*P. 58c).</td><td rowspan="3">White precipitate: $AlCl_3 6H_2O$.</td><td colspan="2">Filtrate. Evaporate, add 10% $NaHCO_3$ solution, boil, pass in H_2S (*P. 58h).</td></tr>
<tr><td>Precipitate: $UO_2NH_4PO_4$. Dissolve in HCl, evaporate, add NaCl and $K_4Fe(CN)_6$ (*P. 58d).
Brown precipitate: $(UO_2)_2Fe(CN)_6$.</td><td>Filtrate: H_3VO_4. Add NH_4OH, saturate with H_2S (*P. 58e).
Red solution: Sulphovanadate. Acidify (*P. 58e).
Black precipitate: V_2S_{4-5}.</td><td>Filtrate. Acidify, boil, add NH_4OH.
White precipitate: $Be(OH)_2$.[1]</td><td>Precipitate: $Al(OH)_3$, Fe_2S_3.</td></tr>
</table>

[1] Filter, and test the precipitate for uranium (*P. 58i).

TABLE IX

ANALYSIS OF THE IRON GROUP FOR THE RARE ELEMENTS, AND FOR THE COMMON ELEMENTS IN THE PRESENCE OF PHOSPHATE

Precipitate from Na_2O_2 treatment: $MnO(OH)_2$, $Fe(OH)_3$, $Tl(OH)_3$, $ZrO(OH)_2$, $TiO(OH)_2$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, $[Zn(OH)_2]$; $CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$; and phosphates of these elements.
Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).

<table>
<tr><td>Brown precipitate: MnO_2.</td><td colspan="4">Solution.[1] Test a portion for iron. To the remainder add NH_4OH till nearly alkaline, then $NH_4C_2H_3O_2$ and $FeCl_3$, dilute, and boil (P. 65).</td></tr>
<tr><td></td><td colspan="3">Precipitate: Basic acetates, hydroxides, and phosphates of Fe, Tl, Zr, Ti. Dissolve in HCl (1.12), shake with ether (*P. 65a).</td><td>Solution: Salts of Co, Ni, Zn, Ca, Sr, Ba, Mg. Add NH_4OH, pass in H_2S (P. 66).</td></tr>
<tr><td></td><td colspan="2">Ether layer: $FeCl_3$, $TlCl_3$. Evaporate, dissolve in dilute H_2SO_4, add KI and Na_2SO_3 (*P. 65d).</td><td colspan="2">Water layer: $TiCl_4$, $ZrCl_4$. Add H_2SO_4, evaporate, add H_2O_2 and Na_2HPO_4 (*P. 65b).</td><td rowspan="2">Precipitate: NiS, CoS, ZnS. See Table VII.</td><td rowspan="2">Filtrate: Salts of Ca, Sr, Ba, Mg.</td></tr>
<tr><td></td><td>Solution: $FeSO_4$.</td><td>Yellow precipitate: TlI.</td><td>White precipitate: $Zr(OH)PO_4$.</td><td>Orange-yellow filtrate: TiO_2. Add Na_2SO_3 (*P. 65c). White precipitate: $Ti(OH)PO_4$.</td></tr>
</table>

[1] Test for phosphate at this point (P. 63); if found absent, make the solution alkaline with NH_4OH (omitting the addition of ammonium acetate and $FeCl_3$), and filter.

Procedures and Notes

Procedure 51. — Boil the filtrate from the H_2S precipitate (P. 21) till the H_2S is expelled. Transfer it to a flask, add NH_4OH (0.96) until the mixture after shaking smells of it, and then 2–4 ccm. more. Note whether there is a precipitate. Add ammonium monosulphide slowly (or if nickel is likely to be present, pass in H_2S) until, after shaking, the vapors in the flask blacken a piece of filter paper moistened with lead acetate solution. To coagulate the precipitate shake the mixture or heat it nearly to boiling. Filter, and wash the precipitate, first with water containing about 1% of the $(NH_4)_2S$ reagent, and then with a little pure water. If the filtration is slow, keep the funnel covered with a watch-glass so as to prevent oxidation. To the filtrate add a few drops $(NH_4)_2S$, boil the mixture for a few seconds, or longer if it is dark colored (till it becomes colorless or light yellow); filter if there is a precipitate, uniting it with the preceding one. (Precipitate, P. 52; filtrate, P. 71, or first by *P. 51*a*, if vanadium is to be tested for.)

Notes. — 1. The H_2S is boiled out and the effect of the addition of NH_4OH alone is noted because it often gives a useful indication as to what elements are present. To save time the expulsion of the H_2S may be omitted when this indication is considered unimportant. Ammonium monosulphide is used, rather than polysulphide, in order to prevent as far as possible the dissolving of NiS, and in order not to introduce sulphur into the precipitate, or polysulphide into the filtrate; for this gives to the filtrate a deep yellow color and causes in the subsequent analysis separation of sulphur on standing or on heating. Excess of the monosulphide is avoided for the same reasons, since it rapidly oxidizes in the air to polysulphide. By passing H_2S into the ammoniacal solution instead of adding $(NH_4)_2S$, the dissolving of NiS is entirely prevented; therefore, though the operation takes a little longer, the use of H_2S is to be preferred when nickel is likely to be present. The mixture is shaken in order to coagulate the precipitate and make it filter more readily. Heating also promotes the coagulation of the precipitate, and it is recommended when the precipitate does not coagulate and settle quickly on shaking. The filtrate is boiled for a few moments to ensure the complete precipitation of $Cr(OH)_3$, or longer to ensure that of NiS, whose presence is indicated by a brown or nearly black color of the filtrate. Finally, it is directed to wash with water containing a little $(NH_4)_2S$, and to keep the filter covered, in order to avoid the oxidation of the sulphides by the air, by which soluble sulphates may be formed.

2. Under the conditions of the procedure, which provides for a small excess of NH_4OH in the presence of NH_4Cl, aluminum, chromium, iron, titanium, zirconium, and beryllium are completely precipitated as hydroxides and uranium as ammonium diuranate, $(NH_4)_2U_2O_7$. All of these precipitates are white, except those of chromium, uranium, and iron. $Cr(OH)_3$ is grayish green and $(NH_4)_2U_2O_7$ is yellow. The color of the precipitated hydroxide of iron varies with the state of oxidation of the iron, pure ferrous salts yielding a white precipitate, and ferric salts a reddish brown one, while mixtures of them yield green or black precipitates. In the alkaline mixtures the precipitate is rapidly oxidized by the oxygen of the air and undergoes corresponding changes in color. Manganous salts are also oxidized rapidly, with the result that brown $Mn(OH)_2$ separates. Under the conditions of the procedure zinc and nickel, when present alone, are completely dissolved; the same is true of cobalt, except when it is present in large quantity; but zinc is precipitated when chromium is also present. The ammoniacal solution of nickel is blue, and that of cobalt of a reddish color, which darkens rapidly on exposure to the air, owing to oxidation. If a smaller excess of NH_4OH is used than is directed, some zinc hydroxide, as well as cobalt hydroxide, may remain undissolved when large amounts of these elements are present, but this has no effect on the subsequent analysis. If, however, a much larger excess of NH_4OH is employed, a few milligrams of aluminum and chromium may be dissolved, the latter giving a pink colored solution.

3. The presence of a considerable quantity of NH_4Cl, such as is formed by the neutralization of the acid already in the solution, serves to prevent the precipitation of $Mg(OH)_2$ [and of $Mn(OH)_2$], and also to lessen the amount of $Al(OH)_3$ dissolved by the NH_4OH.

4. The influence of an excess of the NH_4OH and of the presence of NH_4Cl on the solubilities of the various hydroxides is explained by the mass-action law and ionic theory as follows: In order that any hydroxide, say of the type MO_2H_2, may be precipitated, it is necessary that the product $C_M.C^2_{OH}$ of the concentrations of the ions M^{++} and OH^- in the solution in question attain the value known as the solubility-product. This varies, of course, with the nature of the hydroxide, but for all the elements of the iron group, and also for magnesium, it has so small a value that even in a solution containing in 50 ccm. only 1 mgm. of the element and a slight excess of NH_4OH, the product $C_MC^2_{OH}$ exceeds it, and precipitation results. When, however, much NH_4Cl is also present, this greatly reduces, in virtue of the common-ion effect, the ionization of the NH_4OH and therefore the OH^- concentration in the solution, so that now for certain elements the product

$C_M C^2_{OH}$ does not reach the solubility value, even when C_M is moderately large (say 500 mgm. in 50 ccm.). This is true of magnesium and manganese, but in the cases of aluminum, chromium, and ferric iron the solubility of the hydroxides in water is so slight that even in NH_4Cl solution the solubility is not appreciable.

If these were the only effects involved, the greater the excess of NH_4OH added, the less would be the solubility of any hydroxide; but other influences come into play with certain of the elements. These influences are of two kinds. The first of these is shown by zinc, nickel, and cobalt. In the case of these elements, just as with silver and copper, the excess of ammonia combines with the simple cathion M^{++}, forming complex cathions of the types $M(NH_3)_2^{++}$ and $M(NH_3)_4^{++}$, thereby removing the simple cathion from the solution and making it necessary for more of the hydroxide to dissolve in order to bring back the value of $C_M.C^2_{OH}$ to that of the solubility product. In such a case the presence of NH_4Cl increases the solubility still further, since it greatly decreases C_{OH} and slightly increases C_{NH_4OH} and C_{NH_3}, owing to the common-ion effect on the ionization of the NH_4OH. Chromium also forms similar ammonia complexes, but in much smaller proportion.

The second effect is exhibited in the case of AlO_3H_3. This hydroxide is a so-called amphoteric substance, *i. e.*, is one which behaves both as a base and as an acid in consequence of its being appreciably ionized both into $3(OH^-) + Al^{+++}$ and into $H^+ + AlO_3H_2^-$ (or AlO_2^- and H_2O). With the H^+ arising from the latter form of ionization, the OH^- coming from the excess of NH_4OH combines to form H_2O, thus causing more AlO_3H_3 to dissolve until the value of $C_{AlO_2}.C_H$ again attains that of the solubility product. Since $C_{AlO_2}.C_H = \text{const.}$ in any solution saturated with AlO_3H_3, and since the equilibrium equations $C_H.C_{OH} = K_W$ and $C_{NH_4}C_{OH} = K_B C_{NH_4OH}$ must be satisfied, it follows from combination of these equations that $\frac{C_{AlO_2}}{C_{OH}} = \text{const.}$ and that $C_{AlO_2} = \text{const.} \times \frac{C_{NH_4OH}}{C_{NH_4}}$. The first equation shows that the quantity of aluminum dissolved is proportional to the concentration of hydroxide-ion in the solution, and that therefore it would be much greater in a solution of a largely ionized base like NaOH than in that of a slightly ionized base like NH_4OH. The second equation shows that the solubility in solutions containing NH_4OH and NH_4Cl (or other ammonium salt) is proportional to the ratio of the concentration of the base to that of the salt; so that the presence of ammonium salts tends to neutralize the solvent action of an excess of the hydroxide. All these conclusions are in accordance with the facts. BeO_2H_2 behaves in the same way as AlO_3H_3, forming the cathion Be^{++} and the anion $BeO_2^=$ or $HBeO_2^-$.

5. It follows from the statements in the preceding notes that if NH_4OH produces no precipitate it proves the absence of as much as 1 mgm. of aluminum, iron, beryllium, uranium, titanium, and zirconium; also of chromium, if the mixture is heated to boiling after the addition of NH_4OH. Care must be taken not to overlook a small precipitate which might otherwise escape detection on account of its transparency. The mixture should therefore be well shaken and allowed to stand 2 or 3 minutes in order that the precipitate may collect in flocks. This treatment also oxidizes the iron when present in small quantity, and thus enables it to be more readily detected, for its precipitation in the ferric state is more complete.

6. When phosphate is present, magnesium, calcium, strontium, barium, and manganese may be partially, or even completely, precipitated by NH_4OH. It is therefore necessary, when phosphate is present, to provide for the detection of the alkaline-earth elements in the analysis of this precipitate. The normal phosphates and the monohydrogen phosphates of these elements are difficultly soluble in water, but dissolve readily in acids, owing to the formation in solution of the much more soluble dihydrogen phosphates or of free phosphoric acid; for example, according to the equations:

$$(Ca^{++})_3(PO_4^{\equiv})_2 + 4H^+Cl^- = 2Ca^{++}(Cl^-)_2 + Ca^{++}(H_2PO_4^-)_2;$$
$$Ca^{++}(H_2PO_4^-)_2 + 2H^+Cl^- = Ca^{++}(Cl^-)_2 + H_3PO_4.$$

Upon the addition of sodium or ammonium hydroxide to such a solution the hydrogen-ion in equilibrium with the $H_2PO_4^-$ and H_3PO_4 is removed, and these dissociate into $HPO_4^{\equiv}$ and $PO_4^{\equiv}$, thus causing precipitation of the corresponding salts. When other elements, like iron, forming more insoluble phosphates are also present, it is evident that they will combine with the phosphate radical, thus leaving the alkaline-earth elements in solution. On the other hand, when a soluble carbonate, or a large excess of a strong base, is also present, the alkaline-earth phosphates will be partially converted into carbonates or hydroxides, leaving phosphate in solution.

7. The presence of any other acid radical which forms with the alkaline-earth element salts soluble in dilute acids but insoluble in ammonia may also cause their precipitation at this point. Such radicals are fluoride, borate, oxalate, and hypovanadate. The fluoride will ordinarily have been removed in the evaporation with acids in the preparation of the solution. The borates of the alkaline-earth elements, though somewhat difficultly soluble, are not sufficiently so to cause them to be precipitated, except when present in very large quantity. Oxalate and hypovanadate, even if present, do not make any change necessary

in the usual process of analysis, for in the course of it vanadate and much of the oxalate are separated from the alkaline earths in P. 52, and the remainder of the oxalate is destroyed in P. 61.

*8. Vanadium when present alone in moderate quantity may remain in solution, but when present in large quantity is precipitated by NH_4OH as a dark gray hydroxide, $VO(OH)_2$. This compound corresponds to the state of oxidation (oxide VO_2) to which vanadic acid (oxide V_2O_5) is partially or completely reduced by H_2S. It is an amphoteric substance which forms with acids soluble blue salts such as $VOCl_2$, vanadyl dichloride, and $VOSO_4$, vanadyl sulphate, and with bases hypovanadates such as $Na_2V_2O_5$ and $Na_2V_4O_7$. When other elements of this group are also present the vanadium may be completely precipitated with them, since their hypovanadates and vanadates are in general difficultly soluble substances.

*9. When a base is added to a uranyl salt (for example, UO_2Cl_2), uranyl hydroxide, $UO_2(OH)_2$, is first formed in solution, but this is an amphoteric substance, and it is converted by the excess of base into salts of diuranic acid, $H_2U_2O_7$, of which even the alkali salts are insoluble.

10. $(NH_4)_2S$ precipitates ZnS, MnS, NiS, CoS, and Tl_2S, and converts $Fe(OH)_2$ into FeS, $Fe(OH)_3$ into Fe_2S_3, and $(NH_4)_2U_2O_7$ very slowly into UO_2S. The hydroxides of aluminum, chromium, titanium, zirconium, and beryllium are not affected by the $(NH_4)_2S$. Whether a hydroxide precipitate is converted into a sulphide precipitate or whether the reverse reaction takes place depends on the relative solubilities of the two compounds and on the relative concentrations of sulphide-ion and hydroxide-ion in the solution. Since in the solution the concentration of the sulphide-ion greatly exceeds that of the hydroxide-ion, even difficultly soluble hydroxides would be converted into more soluble sulphides, provided that the difference in solubility is not too great. In the case of hydroxides like $Al(OH)_3$, which are not so changed, their sulphides are so much more soluble that they do not form in aqueous sulphide solutions.

11. The sulphides of iron, nickel, and cobalt are black; Tl_2S and UO_2S are dark brown; ZnS is white; and MnS is flesh-colored, but turns brown on standing in the air, owing to oxidation to hydrated Mn_2O_3.

12. When nickel is present alone, or in large proportion in the $(NH_4)_2S$ precipitate, several milligrams of it usually pass into the filtrate, making it dark-colored, and some NiS also passes through the filter with the wash water. In this case it is useless to try to remove the NiS by filtering again, but it can be coagulated by boiling for several minutes. This behavior of nickel, as stated above, can be avoided

altogether by passing H_2S into the NH_4OH solution to precipitate the sulphide instead of adding $(NH_4)_2S$. The formation of this brown solution depends upon the presence of ammonium polysulphide, for nickel may be completely precipitated by ammonium monosulphide in the absence of air. The nature of the brown solution is not known.

***Procedure 51a.** — To the filtrate from the $(NH_4)_2S$ precipitate (P. 51) add 5 ccm. NH_4OH (0.90) and completely saturate the solution with H_2S. (Pink or violet-red color, presence of VANADIUM.)

If no red color results, boil the solution for several minutes in a casserole to expel most of the NH_4OH and $(NH_4)_2S$, filter off the sulphur, and treat the filtrate by P. 81.

If the solution assumed a pink or red color, acidify it with HCl (1.12), heat it to boiling, and filter. Boil the filtrate in a casserole to expel H_2S, add 0.5–5 ccm. 10% $FeCl_3$ solution, and NH_4OH (0.96) until the mixture after shaking smells of it, and filter. (Filtrate, P. 81.) Heat the HCl precipitate (with the filter, if necessary) with 5–10 ccm. HNO_3 (1.20) until the black precipitate is dissolved, and filter. (If the red coloration produced by H_2S was slight, evaporate the filtrate to about 2 ccm.) Add to the solution a few drops of 3% H_2O_2. (Orange-yellow or orange-red color, presence of VANADIUM.) Dissolve the NH_4OH precipitate by pouring a small portion of HNO_3 (1.20) repeatedly through the filter, and test for vanadium with H_2O_2 in the same way, first adding a little water to the HNO_3 solution if it has a red color owing to the presence of much ferric nitrate.

Notes. — 1. An ammoniacal solution of a vanadate or hypovanadate quickly becomes yellowish red when H_2S is led into it, and this color slowly deepens as more H_2S is absorbed; but the characteristic brilliant violet-red color is obtained only when the solution is completely saturated with H_2S. The presence of ammonium salts tends to prevent the formation of this red compound, but their influence is overcome by the addition of a large excess of NH_4OH. These facts make it probable that this red compound is an ammonium sulphovanadate, from which the sulphur is readily split off as SH^--ion, owing to hydrolysis. Under the conditions of the procedure 0.2 mgm. V can be easily detected, the solution then having a pink color.

2. Upon the addition of HCl the sulphosalt is immediately decomposed, with formation of a black precipitate of V_2S_4 or V_2S_5. This precipitation is far from complete under these conditions, only about half the vanadium being thrown down. More or less sulphur will also

be precipitated, but the dark color of the sulphide is apparent even when less than 0.5 mgm. V is present. Acetic acid may be used instead of HCl, but the proportion of vanadium precipitated as sulphide is not much increased.

3. When a three to fivefold excess of a ferric salt is present and NH_4OH is added, the remainder of the vanadium is precipitated (probably as hypovanadate) together with the $Fe(OH)_3$.

4. The confirmatory test for vanadium with H_2O_2 depends upon the formation of pervanadic acid, HVO_4. 0.1–0.2 mgm. V may be detected in a volume of 5 ccm., provided that the solution is strongly acid. A very large excess of H_2O_2 is to be avoided, for this decreases the intensity of the color, and may even decolorize the solution completely if very little acid is present, probably owing to the formation of a colorless compound of pervanadic acid with hydrogen peroxide.

5. Molybdenum, if not completely precipitated by H_2S in P. 21, and tungsten, if it passed into the original acid solution (owing to the presence of phosphate or arsenate) in P. 3, may also be present in the filtrate from the $(NH_4)_2S$ precipitate. Upon saturating with H_2S molybdenum also gives a deep red color, which would obscure the test for vanadium and might be mistaken for it; but tungsten gives no color. Upon acidification with HCl tungsten divides between the precipitate and filtrate, but molybdenum is thrown down completely as black MoS_3. (If the cold solution is acidified with acetic acid, the sulphomolybdate remains undecomposed for some time and the MoS_3 is not completely precipitated even on boiling.) In the final confirmatory test with H_2O_2 tungsten gives no color; and molybdenum, even when a large quantity is present, gives only a pure yellow color, but not an orange or red one.

Procedure 52. — Transfer the $(NH_4)_2S$ precipitate (P. 51) with the filter, if necessary, to a casserole; add 5–20 ccm. HCl (1.12), stir for a minute or two in the cold, and then boil the mixture for 2 or 3 minutes; if a black residue still remains, add a few drops HNO_3 (1.42) and boil again. Dilute with a little water, filter off the sulphur residue, and evaporate the filtrate to a small volume to remove the excess of acid.

*In order to detect rare-earth elements, and to remove them if present, treat this solution by *P. 52*a*.

*If uranium and vanadium are to be tested for later by *P. 58*a–h*, evaporate twice with a little HNO_3 (1.42) to destroy HCl.

Dilute the solution to 10 or 20 ccm.; make alkaline with NaOH solution, avoiding a great excess; add 10–20 ccm. more water if so

large a precipitate separates that the mixture becomes almost gelatinous. Cool by placing the casserole in cold water and add 0.5–3 grams solid Na_2O_2 in small portions with constant stirring. Then add 5 ccm. 10% Na_2CO_3 solution; boil for 2 or 3 minutes to decompose the excess of Na_2O_2, cool, dilute with an equal volume of water, filter with the help of suction, and wash with hot water. (Precipitate, P. 61; filtrate, P. 53, or, if uranium or vanadium is to be tested for, *P. 58*a*.)

Notes. — 1. All the hydroxides and all the sulphides, except NiS, CoS, usually dissolve readily in cold HCl. If, therefore, there is considerable black residue after adding the HCl, it shows the presence of nickel or cobalt (or possibly vanadium); a very small black residue may, however, be due to FeS enclosed within sulphur. The fact that there is no such dark-colored residue does not, however, prove that nickel and cobalt are absent, for a considerable quantity of them (even 5 mgm.) may dissolve completely in the HCl when large quantities of other elements, especially iron, are also present.

2. The fact that NiS and CoS dissolve so much less readily in dilute acids than do the other sulphides of this group seems to be due not to a lesser solubility in water, but to an unusually slow rate of solution; for nickel and cobalt are not precipitated by H_2S even from a much more weakly acid solution, and their sulphides obtained by precipitation with an alkaline sulphide continue to dissolve in dilute acids without reaching a limit determined by the concentration of the H_2S and the nickel-ion or cobalt-ion in the solution, as would be the case if the phenomenon were that of the solubility of a difficultly soluble sulphide.

3. The $(NH_4)_2S$ precipitate is first treated with HCl, partly in order to furnish the indication just referred to of the presence of nickel or cobalt, but mainly because much more free sulphur and sulphate would be formed by oxidation if HNO_3 or *aqua regia* were used at the start. The presence of the sulphate in considerable quantity in the solution interferes with the subsequent test for chromate [with $Ba(NO_3)_2$ in P. 55 or with $Pb(NO_3)_2$ in *P. 58*b*]. If NiS, CoS, or V_2S_5 are present in the residue, HNO_3 must, however, be subsequently added, to ensure the solution of these sulphides. *The HCl is destroyed by evaporation with HNO_3, since chloride interferes with the test for chromate with $Pb(NO_3)_2$ in *P. 58*b*.

*4. If the $(NH_4)_2S$ precipitate be allowed to stand for a long time before treating it with acid, or if the mixture be heated for a long time after the precipitation, $TiO(OH)_2$ and $ZrO(OH)_2$ may remain in part undissolved even by the boiling concentrated acids, owing to the

fact that the hydroxides at first precipitated become partially dehydrated, in which state they are very difficultly soluble. If this happens at this point, or in dissolving hydroxide precipitates obtained later in the analysis, the residue may be dissolved in a little HF in a platinum dish, and the HF then expelled by evaporating two or three times with HNO_3 (or HCl) nearly to dryness.

5. By NaOH, iron, manganese, nickel, cobalt, *titanium, *zirconium, *thallic thallium, and *uranium are completely precipitated and do not dissolve in moderate excess; while aluminum, chromium, zinc, *vanadium, and *beryllium remain in solution or dissolve when a sufficient excess is added, owing to the fact that their hydroxides are amphoteric substances (see P. 51, Note 3), and form with the NaOH soluble aluminate ($NaAlO_2$), chromite ($NaCrO_2$), zincate (Na_2ZnO_2), vanadate (Na_3VO_4), and beryllate (Na_2BeO_2). Thallium in the thallous state also remains in solution, since TlOH is a readily soluble substance. When zinc and chromium are simultaneously present they are precipitated in the form of a double compound ($ZnCr_2O_4$). Chromium would also be completely precipitated, owing to hydrolysis and the formation of a less soluble solid hydroxide, if the NaOH solution were boiled before adding Na_2O_2. It will be observed that NaOH precipitates manganese, nickel, and cobalt, while NH_4OH does not. This occurs with manganese because of the far greater concentration of hydroxide-ion in the NaOH solution, and with nickel and cobalt partly on this account and partly because there is no complex formation as there is with NH_4OH. $Mn(OH)_2$ is white, but rapidly turns brown, owing to oxidation, to $Mn(OH)_3$; $Ni(OH)_2$ is light green; $Co(OH)_2$ is pink, but from cobalt solution a blue basic salt is first precipitated in the cold. If a large excess of NaOH be added a little $Co(OH)_2$ dissolves, yielding a blue solution, doubtless forming a salt such as Na_2CoO_2. This is to be avoided, since then the cobalt will not be completely oxidized and precipitated upon the subsequent addition of Na_2O_2.

6. By the addition of Na_2O_2, $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$, $Mn(OH)_2$ to brown hydrated MnO_2, $Co(OH)_2$ to black $Co(OH)_3$, $Ni(OH)_2$ partially to black $Ni(OH)_3$, and thallium is precipitated as dark red $Tl(OH)_3$, all of which are insoluble in excess of cold NaOH and remain, together with $TiO(OH)_2$ and $ZrO(OH)_2$, in the precipitate. Chromium and uranium, which after the addition of NaOH are present as soluble sodium chromite or as insoluble sodium diuranate ($Na_2U_2O_7$), are converted by Na_2O_2 into chromate (Na_2CrO_4) and peruranate, which are soluble compounds and remain in solution, together with the zinc, beryllium, and vanadium, which are still present as zincate, beryllate, and vanadate. The separation is more satisfactory,

especially in the case of uranium, when a large amount of Na_2O_2 is used.

7. Even a cold solution of Na_2O_2 decomposes rapidly with evolution of oxygen, and this decomposition takes place with explosive violence when the solution is hot. The peroxide is therefore added in small portions to the cold solution. A steady evolution of gas continuing after the mixture has been well stirred is an indication that sufficient peroxide has been added. The mixture is finally boiled in order to destroy the excess of Na_2O_2 and to cause the complete precipitation of titanium, some of which first passes into solution, probably as the pertitanate. The solution is cooled because $Tl(OH)_3$ is somewhat more soluble in the hot solution than in the cold one. Even in the cold, when thallium is present alone, about 0.5 mgm. will usually pass into the filtrate; but precipitation is complete when elements of the iron group are also present. The solution is diluted before filtering in order to avoid the disintegration of the filter paper; it is often advantageous to support the filter by folding it together with a small, hardened filter.

8. The Na_2CO_3 is added to ensure the complete precipitation of magnesium, calcium, strontium, and barium, whose hydroxides, especially that of barium, are somewhat soluble even in the presence of NaOH. $ZnCO_3$, though insoluble in a dilute solution of Na_2CO_3 alone, dissolves when much NaOH is present, owing to the nearly complete conversion of the zinc-ion into zincate-ion by the reaction $Zn^{++} + 4OH^- = ZnO_2^= + 2H_2O$. The Na_2CO_3 also serves to decompose the chromates of the alkaline-earth elements; if it is not added, chromium may remain in the precipitate and escape detection. It is unnecessary to add the Na_2CO_3 when the alkaline-earth elements are known to be absent.

9. Phosphate or oxalate, if present, divides itself in this procedure between the precipitate and solution in a proportion which depends on the nature and quantities of the metallic elements. (See P. 51, N. 6.) Their presence does not cause any of the elements to precipitate which would not otherwise do so, in spite of the slight solubility of aluminum, zinc, and beryllium phosphates. This is due to the fact that the cathions of these elements (Al^{+++}, Zn^{++}, Be^{++}) are present in the NaOH solution only at an extremely small concentration, owing to their combination with the OH^--ion to form anions (AlO_2^-, $ZnO_2^=$, $BeO_2^=$).

10. Even when less than 1 mgm. Cr is present as chromate, it imparts a distinct yellow color to the alkaline solution, so that when a colorless solution results it proves the absence of this element. Uranium in small quantity also gives a yellow color to the solution, which

is noticeable with 1 or 2 mgm.; a moderate amount (about 10 mgm.) gives a red color, which is intense with still larger quantities. Alkaline solutions containing vanadium are colorless after boiling.

11. This separation with NaOH, Na_2O_2, and Na_2CO_3 is a very satisfactory one, except in the case of zinc. This element, when present in small quantities, is completely carried down in the precipitate when much iron, nickel, or cobalt, or especially manganese, is present. Provision for the detection of zinc in the precipitate must therefore be made.

12. If Na_2O_2 is not available, sodium hypobromite, NaBrO (prepared by mixing NaOH and bromine as described in P. 70, N. 3), may be used as the oxidizing agent; but it is not quite so satisfactory as Na_2O_2, for it does not oxidize $Cr(OH)_3$ so readily, and it is apt to oxidize some of the manganese to $NaMnO_4$ (especially if there is not a sufficient excess of NaOH present).

***Procedure 52a.** — To detect rare-earth elements, and to remove them if present, transfer the acid solution (P. 52) to a platinum dish [after destroying any HNO_3, if any has been added, by evaporating in porcelain once or twice with HCl (1.20)], and evaporate just to dryness. Add to the residue 45% HF solution, little by little, until the residue has been dissolved, or until about 25 ccm. have been added, stirring with a platinum rod after each addition, and finally boiling gently under a hood for a minute or two if there is still a residue. Collect the residue on a filter supported on a platinum ring or in a celluloid funnel; collect the filtrate in a platinum dish; wash the residue thoroughly with water.

To the filtrate add 3–5 ccm. HCl (1.20), and evaporate it just to dryness; add a little HCl and evaporate again, and repeat these operations a third time. Dissolve the residue in a little water, adding HCl if necessary; transfer to a casserole, and treat the solution by the last paragraph of P. 52, first evaporating with HNO_3 to destroy HCl if chromium, uranium, and vanadium are to be tested for by *P. 58*a–e*.

Transfer the residue insoluble in HF to a platinum crucible; if the filter has been added, ignite to destroy it. Add 2–5 ccm. H_2SO_4 (1.20), heat until sulphuric acid fumes are given off, cool, add 10–20 ccm. water, heat, and filter. Treat the precipitate (which can consist only of $CaSO_4$, $SrSO_4$, or $BaSO_4$) with concentrated Na_2CO_3 solution by P. 6. To the H_2SO_4 solution add ammonia until alkaline. (White precipitate, presence of RARE-EARTH ELEMENTS.) Filter and test the filtrate for

calcium and magnesium. Wash the precipitate thoroughly, dissolve it in a little HCl, evaporate just to dryness in a platinum dish, dissolve in a little water, and add 5–10 ccm. HF. (White precipitate, presence of RARE-EARTH ELEMENTS.)

Notes. — 1. Among the so-called rare-earth elements are included thorium, cerium, lanthanum, praseodymium, neodymium, yttrium, ytterbium, and a number of other similar elements. These elements, like the alkali-earth elements, are characterized by the insolubility of their fluorides, but differ from the alkali-earth elements in that their hydroxides are precipitated by ammonia and that their sulphates are not precipitated by sulphuric acid. It is upon these facts that the separation described in the above procedure is based. If there is no residue after the treatment with HF, it shows, of course, that the rare-earth elements are absent; if, on the other hand, there is a residue, it does not necessarily show their presence, except when it is known that alkaline-earth elements cannot be present. (See P. 51, N. 6 and 7.) The further treatment described in the procedure serves to eliminate the latter.

2. Owing to the fact that aluminum and chromium fluorides are somewhat difficultly soluble in HF, care must be taken to use a rather large quantity of this acid when a residue remains. It is also obvious that the fluoride residue must be thoroughly washed if the formation of a precipitate with ammonia is to be considered a conclusive indication of rare-earth elements. The final treatment of the NH_4OH precipitate is recommended to eliminate the possibility of error from these sources.

3. The HF solution, which may contain all the elements of the aluminum and iron groups, is evaporated repeatedly with HCl to expel the HF, which is especially apt to be retained when titanium and zirconium are present.

The Aluminum Group

Procedure 53. — Acidify the alkaline solution (P. 52) with HNO_3 (1.42), avoiding a large excess; add NH_4OH (0.96) until the mixture after shaking smells of it, and then add 2–3 ccm. more. Heat almost to boiling in order to coagulate the precipitate, filter, and wash thoroughly with hot water. (White flocculent precipitate, presence of ALUMINUM (or *BERYLLIUM); colorless solution, *absence* of CHROMIUM.) (Precipitate, P. 54, or to detect beryllium, *P. 58*g* and *h*; filtrate, P. 55.)

Notes. — 1. The alkaline solution is acidified with HNO_3, instead of with HCl, because the latter acid might reduce chromic acid, especially if a large quantity were added, or if the acid solution were heated. A moderate excess of NH_4OH must be added in order to keep the zinc in solution, which it does because of the production of $Zn(NH_3)_4^{++}(NO_3^-)_2$; but a large excess is to be avoided, since it dissolves $Al(OH)_3$, owing to formation of $NH_4^+AlO_2^-$. The zinc is dissolved even when carbonate, phosphate, or oxalate is present.

2. Since aluminum and silica are very likely to be present in the NaOH and Na_2O_2 used as reagents, and since they may be taken up from the dishes, a blank test for these impurities should be made whenever new reagents are employed for the first time by following P. 52 and 53 and comparing the NH_4OH precipitate with that obtained in any regular analysis. It is also well at the same time to test for zinc by acidifying the NH_4OH solution with acetic acid and following P. 57.

Procedure 54. — Dissolve the precipitate (P. 53), or a small portion of it if it is large, in 5 ccm. HNO_3 (1.20). From the appearance of the precipitate estimate the number of milligrams of aluminum which have been dissolved, and to the solution add about one-fourth as much cobalt as cobalt nitrate, using, however, not less than 0.2 mgm. Evaporate almost to dryness in a casserole, add a drop or two of water, and soak up the solution in a small piece of filter paper. Make a small roll of the paper, wind a platinum wire around it to form a spiral, and incinerate the paper in a small flame, finally heating the residue strongly. (Blue residue, presence of ALUMINUM.)

Notes. — 1. A confirmatory test for aluminum should always be tried when the NH_4OH precipitate is small, for general reasons, inasmuch as the precipitation by NH_4OH of an element whose hydroxide is soluble in NaOH is not very characteristic (lead, antimony, tin, and beryllium showing a similar behavior), but also especially to guard against mistaking SiO_3H_2 for $Al(OH)_3$; for the former substance, if not entirely removed by proper dehydration in the process of the preparation of the solution (in P. 3, Part I), may appear at this point. A gelatinous precipitate which does not dissolve in HNO_3 indicates silica; it may be tested for by P. 5.

2. The test described in this procedure depends upon the formation of a blue compound, whose formula is not definitely known; but it is doubtless a compound of the two oxides $CoO.xAl_2O_3$, and may be simply cobalt aluminate, $Co(AlO_2)_2$. It may be formed in various ways; but the process described in the procedure seems to be the most suitable

one for making the test for aluminum reliable and delicate. It is of the utmost importance to have the aluminum present in excess; for otherwise the blue color is obscured by the black oxide of cobalt. In order that a small enough amount of cobalt may be added, it is convenient to use a very dilute solution of cobalt nitrate, say one that contains one-tenth of a milligram of cobalt per cubic centimeter.

3. When the test is properly made, the ash retains the form in which the filter paper was rolled, and the whole mass, or a large part of it, is colored blue. The presence of an equivalent amount of phosphate does not spoil the test. When, however, sodium or potassium salts are present, the ash fuses together and the test is very unsatisfactory. For this reason the sodium salts present should be all washed out of the NH_4OH precipitate before dissolving it in HNO_3. No other element gives a blue color to the ash; but certain elements, especially iron, obscure the test, so that it can be applied only after other elements have been removed in the regular process of analysis. 0.5 mgm. Al may be easily detected, and even 0.2 mgm. after a little practice.

4. Another very good confirmatory test for aluminum consists in dissolving the NH_4OH precipitate in HCl (1.12), adding 1½ volumes of ether, and saturating the mixture in the cold with HCl gas, as described in *P. 58*g*. Under these conditions aluminum separates in the form of the crystalline compound $AlCl_3.6H_2O$; but no other element of the aluminum group is precipitated, except chromium, which if present in quantity greater than 10–20 mgm. gives a violet precipitate. Moreover, silica does not interfere with this test. By this process, moreover, beryllium is quantitatively separated from aluminum, and may be tested for in the filtrate.

Procedure 55. — Acidify the NH_4OH solution (P. 53) with 30% acetic acid solution, avoiding an excess of more than 2 ccm.

If the solution is colorless, treat it by P. 57.

If it is at all yellow, add about 10 ccm. 10% $BaCl_2$ solution, allow the mixture to stand for at least 5 minutes, and filter. (Yellow precipitate, presence of CHROMIUM.) (Precipitate, P. 56; filtrate, P. 57.)

Notes. — 1. The presence of less than 0.5 mgm. chromium as chromate in a volume of 50 ccm. makes the solution distinctly yellow, and the addition of $BaCl_2$ is therefore unnecessary when the solution is perfectly colorless. It is to be avoided, since $BaSO_4$ may be precipitated and has then to be removed by filtration. In doubtful cases the color of the solution should be compared with that of water. The color test is, of course, not delicate by artificial light.

2. Since some sulphate may be present, the formation of a white precipitate with $BaCl_2$ does not prove the presence of chromium. Whether the precipitate is pure white or yellow should therefore be carefully noted. The yellow color of a small $BaCrO_4$ precipitate is most apparent when the precipitate has settled or when it has been collected on the filter. If there be sufficient sulphate present to obscure the yellow color of a little $BaCrO_4$, the confirmatory test for chromium described in the next procedure should be tried.

Procedure 56. — Pour repeatedly through the filter (P. 55) a 5–10 ccm. portion of a mixture of 1 volume of HNO_3 (1.20) with 9 volumes of water; to the cold solution in a test tube add about 2 ccm. of ether and 1 ccm. 3% H_2O_2, and shake. (Blue coloration of ether layer, presence of CHROMIUM.)

Note. — This blue compound which is formed by the action of H_2O_2 on chromic acid is one of the perchromic acids. It has the formula H_3CrO_7, and appears to be an addition product of H_2O_2 and a higher oxide of chromium. It is a very unstable substance; by its decomposition oxygen is evolved and the chromium is reduced to a trivalent chromic salt. Its decomposition is greatly accelerated by an excess of H_2O_2, by the presence of much acid, and by raising the temperature. It is therefore important not to add too much H_2O_2, and to use dilute acid, as directed in the procedure. If in dissolving the precipitate the filter be heated with HNO_3, the paper causes the chromate to be reduced to a chromic salt; but when the cold acid is merely poured through the filter this reduction does not take place. If a green solution should be obtained, the chromium must be reoxidized with Na_2O_2 in alkaline solution before making the test. Under proper conditions 0.2 mgm. Cr may be detected, but the test may fail with a much larger amount if the directions are not followed.

Procedure 57. — Warm the acetic acid solution (P. 55 or *P. 58*f*) to 50° or 60°, saturate it in a small flask with H_2S, cork the flask, and allow it to stand for 5 or 10 minutes if no precipitate separates at once. (White flocculent precipitate, presence of ZINC.) Filter through a double filter (two filters folded together); wash once with a little water. Reject the filtrate.

To confirm the presence of zinc, pour a 5–10 ccm. portion of HNO_3 (1.20) two or three times through the filter containing the H_2S precipitate. To the solution add an amount of cobalt as cobalt nitrate equal to about one-fourth of the amount of zinc estimated to be present,

using, however, not less than 0.2 mgm. cobalt. Evaporate in a casserole almost to dryness to expel the acid, neutralize with 10% Na_2CO_3 solution, and add about 0.5–1 ccm. in excess. Evaporate to dryness, ignite gently until the purple color due to the cobalt disappears, and allow the casserole to cool. (Green color, presence of ZINC.)

Notes. — 1. ZnS precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mgm.) may be missed unless a short time be allowed for the precipitate to coagulate; but since sulphur may then separate, the appearance of a white turbidity is not sufficient proof of the presence of zinc. The precipitate may be allowed to settle in order that the amount of zinc present may be better estimated. A double filter is used, since the ZnS is apt to pass through the filter.

2. The immediate formation of a white flocculent precipitate with H_2S in acetic acid solution is so characteristic as to be a sufficient test for zinc. Manganese is the only other element of this group that forms a light-colored sulphide; and this, owing to its greater solubility in water, does not precipitate from an acetic acid solution. The confirmatory test described in the last paragraph of the procedure is, however, useful when only a small noncoagulating precipitate which may be sulphur results, or when, owing to the presence of a small quantity of other elements, the precipitate is dark-colored.

3. The green compound obtained in the confirmatory test is doubtless a compound of cobalt and zinc oxides, perhaps cobalt zincate, $CoZnO_2$. The conditions under which the zinc and aluminum compounds of cobalt are formed are very different. As we have seen, the aluminum compound is formed only at very high temperatures, and the test is not at all delicate in the presence of a salt of an alkali element. On the other hand, the zinc compound is obtained at comparatively low temperatures, and the presence of an alkali is essential. Excess of cobalt must, of course, be avoided, for the black cobalt oxide completely obscures the green color. A larger proportion of cobalt than is recommended in the procedure may be added without danger, but the test is very satisfactory even when a large excess of zinc is present.

***Procedure 58a.** — To the filtrate from the Na_2O_2 precipitate (P. 52) add HNO_3 (1.20), keeping the solution cool, until it reacts slightly acid and any precipitate just redissolves upon shaking. (See N. 1.) Dilute the solution to 100 ccm. and transfer it to a strong 200 ccm. bottle. Add solid $NaHCO_3$, a little at a time, until the mixture after shaking no longer turns blue litmus paper red at once;

finally add 1.0–1.5 grams solid $NaHCO_3$ (weighed out roughly). Close the bottle with a tightly fitting cork, wire it in, wrap a cloth around the bottle, place it in a vessel of warm water, and boil the water gently for 20 or 30 minutes. Cool the bottle to at least 50° (best by slowly adding cold water to the bath), remove the cork, filter at once, and wash, using suction if the precipitate is large. (Filtrate, *P. 58*b*; precipitate, *P. 58*f*.)

Notes. — 1. If up to this point in the analysis there has been no indication of any of the elements that are to be tested for in the alkaline solution, time may often be saved by determining before treating with $NaHCO_3$ whether any of them are present by proceeding as follows: to one-fourth of the solution, which has been acidified with HNO_3, add NH_4OH (0.96) in small excess, note whether a precipitate forms, and then add a few drops of $(NH_4)_2S$ solution. Even if there is no precipitate, vanadium may be present; to test for this, add 3 ccm. NH_4OH (0.90) and completely saturate with H_2S. (See *P. 51*a*.) If the results of these tests show that any of these elements are present, treat the remainder of the HNO_3 solution by the regular procedure. If, on the other hand, the results are negative, no further treatment is necessary.

2. The alkaline solution is kept cold during the neutralization, and an excess of HNO_3 is avoided because chromate in the presence of H_2O_2 and an acid is rapidly reduced to a chromic salt, especially when the solution is hot. This reduction, if complete, would prevent the detection of chromium in the subsequent test. H_2O_2 will, to be sure, not be present, since Na_2O_2 is very rapidly destroyed by the boiling of the alkaline solution in P. 52, except when uranium is also present; in this case the peruranate which is formed by the treatment with Na_2O_2 is not decomposed upon boiling, but breaks up into a uranyl salt and H_2O_2 upon acidification.

3. The success of this separation depends upon securing the proper concentration of the $NaHCO_3$. Since the $NaHCO_3$ may be at first used up in precipitating zinc, aluminum, and beryllium, as well as in neutralizing the free acid, the weighed amount of $NaHCO_3$ is added only after the solution ceases to react distinctly acid. A much larger concentration of $NaHCO_3$ than 1.0–1.5% would not prevent the complete precipitation of zinc or of aluminum, but it would interfere with that of beryllium. Thus with a volume of 100 ccm. the precipitation of the beryllium is complete when the concentration of the $NaHCO_3$ is 1%, and 1 mgm. can usually be detected when it is 2%; but 3 mgm. remain dissolved in a 3% solution, about 15 mgm. in a 5% solution, and about 150 mgm. in a 10% solution. A smaller concentration of

$NaHCO_3$ and a smaller volume than 100 ccm. are avoided, in order to prevent as far as possible the precipitation of uranyl vanadate, which may otherwise occur when large quantities of uranium and vanadium (about 100 mgm. of each) are simultaneously present. The presence of phosphate or oxalate (or chromate) does not cause the precipitation of uranium, nor otherwise interfere with the analysis. When only small amounts of the elements of this group are present the separation can be made in a smaller volume, care being taken that the concentration of the $NaHCO_3$, rather than the quantity taken, be that prescribed.

4. If it is desired, the separation may be made in an open flask; but in this case the solution must not be boiled and the $NaHCO_3$ solution should not be stronger than 1%. The process is then best carried out by digesting the mixture on a water bath for 20–30 minutes in a flask covered with a watch-glass. Under these conditions neither zinc nor beryllium dissolves in significant quantity, but 1–2 mgm. of aluminum may be completely dissolved. The mixture must not be boiled, for a larger amount of aluminum may then dissolve (as much as 5 mgm. on 1 minute's boiling).

5. When a large amount of aluminum or beryllium is present, 2–5 mgm. of uranium may be carried down almost completely in the $NaHCO_3$ precipitate, so that in this case uranium has to be tested for in the analysis of the precipitate.

6. In a dilute solution of $NaHCO_3$ saturated with CO_2 the hydrogen-ion and hydroxyl-ion concentrations are both very small and are nearly the same as in pure water. AlO_3H_3, basic $BeCO_3$, and $ZnCO_3$ are completely precipitated because the solubility of these substances is not much increased through removal of the OH^- or $CO_3^=$ by combination with H^+ with formation of H_2O or HCO_3^- (leaving the cathions Al^{+++}, Be^{++}, or Zn^{++} in the solution), or through removal of the metal-ions by combination with the OH^- with the formation of AlO_2^-, $BeO_2^=$, or $ZnO_2^=$. The higher hydroxides of chromium and vanadium (chromic and vanadic acids) are soluble, polybasic acids, which are so much more highly ionized than H_2CO_3 that they displace it from its salt, $NaHCO_3$, forming mainly sodium hydrogen chromate or vanadate. The fact that uranium is not precipitated, even though $Na_2U_2O_7$ is difficultly soluble, may be due to the formation of a complex sodium uranyl carbonate.

***Procedure 58b.** — To the $NaHCO_3$ filtrate add HNO_3 (1.20) until the solution is distinctly acid, avoiding an excess of more than 1 ccm. (Colorless solution, absence of CHROMIUM.) Unless the solution is as colorless as pure water, test one-fourth of it for chromium by adding to the cold solution in a test tube 2 ccm. ether and 0.5–1.0 ccm. 3%

H_2O_2 solution. (Blue coloration of the ether layer, presence of CHROMIUM.) To this mixture add about 5 ccm. HNO_3 (1.42). (Red coloration of water layer, presence of VANADIUM.)

If chromium is not present, treat the HNO_3 solution or the part of it not tested with H_2O_2 by *P. 58*c*.

If chromium is present, exactly neutralize the remainder of the HNO_3 solution with NaOH, add 2 ccm. HNO_3 (1.20) and then 20 ccm. 20% $Pb(NO_3)_2$ solution; allow the mixture to stand for 15–20 minutes, and filter. (Yellow precipitate, presence of CHROMIUM.) Saturate the filtrate with H_2S, filter off and reject the precipitate; boil the filtrate for 2 or 3 minutes to expel H_2S and to coagulate any sulphur that may separate; filter off and reject the precipitate. In order to oxidize vanadyl salts to vanadate add bromine water (or, if much is required, liquid bromine) until the solution has a permanent reddish color. Boil in a casserole until the bromine is expelled and treat the solution by *P. 58*c*.

Notes. — 1. The $NaHCO_3$ filtrate should not be heated after acidifying, because some H_2O_2 may still be present (even though most of it is decomposed in the heating with $NaHCO_3$), which would cause the reduction of chromate, and might thus prevent the detection of even several milligrams of chromium. (See *P. 58*a*, N. 2.)

2. It is desirable to determine in advance, by making a preliminary test if necessary, whether or not chromium is present; for if it is absent, the addition of the lead salt and the subsequent removal of the lead with H_2S may be omitted. If added, its removal is necessary before the tests for uranium and vanadium can be made. If the acid solution is perfectly colorless, an amount of chromium exceeding 0.5 mgm. may safely be pronounced absent. Uranium and especially vanadium in moderate quantity (20–50 mgm.) also give yellow solutions. A yellow solution is therefore tested for chromate with H_2O_2. In regard to this test, see P. 56, N. 1. The test can be made in only a small portion (one-fourth) of the solution; for it is so delicate that the presence of 0.1 mgm. chromium in this portion can be detected. The portion in which the test is made is rejected, because chromium, if present, is reduced to the chromic state by the H_2O_2 in the acid solution, and would therefore not be precipitated by the lead nitrate.

3. When vanadium is present, even in moderately small quantity, the water layer, on the addition of H_2O_2, becomes orange-yellow to orange-red in color, owing to the formation of pervanadic acid. This test for vanadium becomes more delicate when the solution is made strongly acid as is directed; a distinct color is then obtained even when

only 0.5 mgm. vanadium is present in the portion tested, corresponding to about 2 mgm. in the whole solution. (Compare *P. 51*a*, N. 4.) The test is not essential, since vanadium is always tested for later; it is introduced here, where it can be made in a moment's time, as an additional confirmation of the presence or absence of that element.

4. The separation of chromium from vanadium and uranium by $Pb(NO_3)_2$ depends on the relatively small solubility of lead chromate in dilute HNO_3 in the presence of a large quantity of $Pb(NO_3)_2$. Under the conditions described in the procedure, over 100 mgm. of vanadium yield no precipitate, and only 0.1–0.3 mgm. of chromium usually remains in solution, though this amount is somewhat increased when a very large quantity of $NaNO_3$ has been introduced. To secure these results, however, care must be taken to use the prescribed quantities of HNO_3 and $Pb(NO_3)_2$, for lead vanadate is also a difficultly soluble substance, and would be quantitatively precipitated in the presence of a much weaker acid, such as acetic acid in the presence of ammonium acetate. Lead uranate would also be precipitated from a neutral or slightly alkaline solution.

5. The presence of much chloride or sulphate would cause the precipitation of white $PbCl_2$ or $PbSO_4$, which might obscure the yellow color of a small quantity of $PbCrO_4$ and prevent the estimation of the amount of chromium present. These anions will, however, not be present in harmful quantity if in dissolving the original $(NH_4)_2S$ precipitate (P. 51) the acids are used in the way prescribed, and if in acidifying the solutions in *P. 58*a* and *b* HNO_3 and not HCl is used, as directed.

6. The lead which is added to precipitate the chromate must be removed before testing for uranium with Na_2HPO_4 (in *P. 58*c*), since it would give a precipitate of $Pb_3(PO_4)_2$. It is precipitated with H_2S, rather than with $(NH_4)_2SO_4$, because in the latter case enough lead (about 1 mgm.) still remains in solution to give a precipitate with Na_2HPO_4.

7. By the H_2S vanadic acid is reduced to vanadyl nitrate, $VO(NO_3)_2$, slowly in the cold, but more rapidly on heating the solution, so that sulphur may be precipitated on boiling the filtrate to expel H_2S. This must be reoxidized to vanadic acid, for otherwise vanadyl ammonium phosphate would be precipitated with the uranium phosphate in *P. 58*c*. The oxidation by bromine does not take place instantaneously; and a considerable excess of bromine must therefore be used and the mixture allowed to stand a few minutes.

***Procedure 58c.** — Make the solution obtained in *P. 58*b* neutral with NH_4OH, add 5 ccm. 30% acetic acid, 1–2 grams solid $(NH_4)_2SO_4$

(or NH_4NO_3), and then 2 grams solid $Na_2HPO_4 12H_2O$, and heat to boiling. (White precipitate, presence of URANIUM.) Allow the mixture to stand for 10–15 minutes to coagulate the precipitate, filter, and wash the precipitate with a 5–10% solution of $(NH_4)_2SO_4$ (or NH_4NO_3). (Precipitate, *P. 58*d*; filtrate, *P. 58*e*.)

Notes. — 1. The precipitation of white uranyl ammonium phosphate, $UO_2NH_4PO_4$, is a delicate test, provided the solution be made only moderately acid with acetic acid and a sufficient excess of Na_2HPO_4 be added. The separation from vanadium as vanadic acid is a very satisfactory one; for vanadium, even when present in large quantity (100 mgm.), does not precipitate, nor is a small quantity carried down by uranium; on the other hand, 0.5 mgm. uranium gives a distinct precipitate. The test is a somewhat more delicate one if made in a smaller volume, say 40 ccm.; in this case the same quantities of reagents may still be used, and the separation is perfectly satisfactory.

2. The formation of a precipitate at this point is not sufficient evidence of the presence of uranium; for aluminum, beryllium, and lead will separate as phosphates if they have not been completely removed in previous procedures, and vanadium will precipitate as vanadyl ammonium phosphate if the oxidation by bromine was incomplete. On the other hand, a slight turbidity may correspond to an appreciable amount of uranium (0.2 to 0.5 mgm.). Therefore the confirmatory test for uranium (*P. 58*d*) should always be tried.

3. When the solution is made alkaline with NH_4OH, a pale yellow precipitate of uranyl ammonium vanadate may separate, and may not dissolve when the acetic acid is added. This, however, has no effect on the separation, since on boiling it is converted into the less soluble uranyl ammonium phosphate and vanadic acid.

4. In the absence of ammonium salts uranium is precipitated as uranyl hydrogen phosphate, UO_2HPO_4, which often separates as a very finely divided precipitate that runs through the filter. The ammonium salt is added to cause the uranium to precipitate as uranyl ammonium phosphate, which coagulates and filters more readily.

***Procedure 58d.** — Dissolve the $NaHPO_4$ precipitate (*P. 58*c*) by pouring a small portion of hot HCl (1.12) repeatedly through the filter, evaporate the solution nearly to dryness, add about 10 ccm. nearly saturated NaCl solution, pour into a test tube, cool, and add 5 ccm. 10% $K_4Fe(CN)_6$ solution. (Dark red precipitate or coloration, presence of URANIUM.)

Note. — The precipitation of the dark red uranyl ferrocyanide $(UO_2)_2Fe(CN)_6$ is a very characteristic and also a very delicate test for uranium, provided care be taken to avoid any excess of acid. The solution must, however, be distinctly acid, for otherwise the precipitate may not form, owing to the small concentration of the uranyl-ion, UO_2^{++}. Uranyl ferrocyanide tends to form a colloidal solution; but the presence of NaCl and HCl soon causes it to coagulate.

***Procedure 58e.** — Neutralize the filtrate from the Na_2HPO_4 precipitate (*P. 58*c*) with NH_4OH (0.90), and add about 5 ccm. more. Saturate the solution completely with H_2S by passing the gas through it in a small flask for 10 or 15 minutes. (Pink or violet-red color, presence of VANADIUM.) Pour the solution through a filter; if it has a pink or red color make it distinctly acid with acetic acid (or HCl) and heat nearly to boiling. (Dark precipitate, presence of VANADIUM.)

Note. — In regard to the formation of the sulphovanadate of vanadium in the strongly alkaline solution, the partial precipitation of vanadium sulphide on acidifying, and a confirmatory test for vanadium by the action of H_2O_2 on vanadic acid, see the Notes on *P. 51*a*.

***Procedure 58f.** — Heat the $NaHCO_3$ precipitate (*P. 58*a*) with 10–30 ccm. HCl (1.06) in a casserole, or dissolve it by pouring the acid two or three times through the filter, boil the solution to expel CO_2, and add NH_4OH (0.96) until the solution after shaking smells of it, and then 2–3 ccm. in excess. Heat the mixture nearly to boiling, filter, and wash the precipitate, using suction if it seems desirable. (Precipitate, *P. 58*g*; filtrate, acidify with acetic acid, and test for zinc by P. 57.)

Note. — The zinc remains in the ammoniacal filtrate as a complex ammonia salt, chiefly $Zn(NH_3)_4^{++}Cl_2^-$. Aluminum and beryllium are precipitated as hydroxides. The precipitate will also contain any uranyl vanadate that was precipitated in the $NaHCO_3$ separation.

***Procedure 58g.** — Dissolve the NH_4OH precipitate (*P. 58*f*) by pouring a hot 5–15 ccm. portion of HCl (1.12) repeatedly through the filter, using another portion of acid if necessary. Add a volume of ether equal to one and one-half times that of the solution. Pass into the mixture in a small flask HCl gas until a single layer results, and until fumes of HCl are copiously evolved, cooling the flask in running water during the process. Cover the flask, and let the mixture stand

for 15 minutes even if no precipitate has separated. (White crystalline precipitate, presence of ALUMINUM.) Filter through an asbestos filter (see P. 61) or through an ordinary filter supported by a small, hardened filter folded with it, after first moistening the filter with a mixture of 2 volumes of HCl (1.20) and 3 of ether previously saturated with HCl gas; wash the precipitate once with this mixture. During the filtration and washing keep the funnel covered with a watch-glass to prevent evaporation of the ether. (Precipitate, P. 54, to confirm the presence of aluminum; filtrate, *P. 58*h*.)

Notes. — 1. Aluminum chloride, $AlCl_3.6H_2O$, is only slightly soluble in concentrated HCl solutions, and the precipitate is complete when ether is added and the mixture saturated with HCl. 0.5 mgm. of aluminum can be easily detected in 30 ccm. The test is therefore a delicate one. It is also very characteristic, for no other element of the aluminum group is precipitated by this treatment, except chromium when it is present in moderate quantity.

2. The ethereal solution of HCl, unlike the concentrated aqueous solution, does not disintegrate filter paper rapidly, and the filtration can almost always be made with an ordinary filter supported by means of a hardened filter. This filtration is apt to be slow, and it is often advantageous to filter through asbestos with the help of suction.

3. When the NH_4OH precipitate is small (corresponding to less than 30 mgm. Al), it need not be treated by this procedure, but it may be dissolved in a little HCl and treated directly by *P. 58*h*.

Procedure 58h. — Evaporate the filtrate from the HCl precipitate (*P. 58*g*), first on a water bath under a hood until the ether is expelled, and then over a flame, almost to dryness until nearly all the HCl is expelled; add a little water, make alkaline with NH_4OH, avoiding a large excess, and heat nearly to boiling. (No precipitate, absence of BERYLLIUM.)

If there is a precipitate, dilute to 30 ccm., add enough solid $NaHCO_3$ to make a 10% solution, heat to boiling, boil for 1 minute, cool, pass in H_2S for a few seconds, and filter after a few minutes if there is a precipitate. Acidify the filtrate with HCl, boil for 2 or 3 minutes to expel CO_2, make the solution alkaline with NH_4OH, and heat nearly to boiling. (White flocculent precipitate, presence of BERYLLIUM; yellow precipitate, presence of URANIUM.)

Treat this precipitate or a portion of it corresponding to about 20 mgm. of beryllium by *P. 58*d*. (Dark red precipitate, presence

of URANIUM.) Filter, and to the filtrate add NH_4OH. (White precipitate, presence of BERYLLIUM.)

Notes. — 1. The filtrate from the HCl precipitate may contain, besides beryllium, uranium or vanadium (carried down in the treatment with dilute $NaHCO_3$ in *P. 58*a*), aluminum (if care was not taken in precipitating and filtering aluminum chloride), and a little iron (introduced from the reagents). This solution is first tested with NH_4OH to determine if any further treatment is necessary. The treatment with the hot concentrated $NaHCO_3$ solution serves to precipitate the aluminum completely and to dissolve the beryllium and uranium. This method of separation of aluminum and beryllium is a satisfactory one when, as in the present case, only a small amount of aluminum is present; a large quantity of aluminum, however, retains almost completely a small quantity of beryllium. The $NaHCO_3$ solution must not be boiled for a long time, because, owing to the escape of CO_2 and the formation of free NaOH, the solution becomes alkaline enough to dissolve some aluminum. The reason for the great solubility of beryllium hydroxide in concentrated $NaHCO_3$ solutions is not known. H_2S is passed in to remove the iron, since a small amount of it remains dissolved in the concentrated $NaHCO_3$ solution. The filtrate is sometimes dark green even after repeated filtration owing to the presence of colloidal iron sulphide; to precipitate this, add a small amount of a ferrous salt (say 2–4 mgm. Fe), shake, allow the mixture to stand several minutes, and then filter, passing more H_2S into the filtrate to make sure that the iron has been all removed.

2. The treatment with $K_4Fe(CN)_6$ described in *P. 58*d* gives a satisfactory separation of beryllium from uranium (and vanadium) provided the amount of beryllium in the solution does not exceed 20 mgm. When more beryllium is present a gelatinous precipitate separates; on this account it is directed to use only a portion of the NH_4OH precipitate when it is large, but even in this case a small amount of uranium can still be detected, owing to the delicacy of the ferrocyanide test. Vanadium, if present, owing to its having been precipitated as uranyl vanadate in the treatment with dilute $NaHCO_3$ (*P. 58*a*), remains with uranium and is precipitated as greenish yellow vanadyl ferrocyanide, but does not obscure the dark red color of the uranium precipitate. It is not necessary to provide for the detection of vanadium at this point, since a large quantity always dissolves in the $NaHCO_3$ treatment.

The Iron Group

Procedure 61. — Transfer the Na_2O_2 precipitate (P. 52) to a casserole, together with the filter if necessary, add 5–30 ccm. HCl (1.12), boil gently till the precipitate is dissolved, filter to remove the paper, and evaporate the filtrate to 1 or 2 ccm. To decompose the HCl, add about 5 ccm. HNO_3 (1.42), and boil as long as oxides of nitrogen are given off. Add 5–20 ccm. HNO_3 (1.42), heat to boiling, add about 0.5 gram of solid $KClO_3$ and boil gently, adding more $KClO_3$ in small portions if a large precipitate forms. (Dark brown or black precipitate, presence of MANGANESE.) Boil gently for a minute or two, and filter through an asbestos filter, made by pouring a suspension of washed asbestos over a compact wad of glass wool in a glass funnel. (See Note 4.) Heat the filtrate to boiling, add more $KClO_3$, boil, and filter through the same filter if more of the precipitate separates. Wash two or three times with HNO_3 (1.42) which has previously been freed from the oxides of nitrogen by warming with a little $KClO_3$. Evaporate the filtrate to about 5 ccm., but not further, dilute to 20 or 30 ccm., and filter the solution if it is turbid. (Precipitate, P. 62; filtrate, P. 63.)

Notes. — 1. HCl is used for dissolving the Na_2O_2 precipitate rather than HNO_3. Pure concentrated HNO_3 does not dissolve hydrated MnO_2 except in the presence of filter paper, whereby the HNO_3 is reduced to lower oxides; the action is more rapid with HCl (for the MnO_2 is thereby quickly reduced to manganous chloride with evolution of chlorine).

2. By $HClO_3$ in HNO_3 solution (but not by HNO_3 alone) manganous salts are rapidly oxidized to hydrated MnO_2 with formation of chlorine dioxide (ClO_2), which escapes as a yellow gas. The HCl must previously be completely removed by evaporation and boiling with HNO_3, since the oxides of nitrogen resulting from its action on the HNO_3 would continuously dissolve the precipitate.

3. The separation of manganese in this way from the other metals of this group is entirely satisfactory with the following exceptions. A small quantity of iron (up to 1 mgm.) may be completely carried down with a large quantity (500 mgm.) of manganese. The same is true in a much higher degree of titanium, of which even 50 mgm. may be entirely precipitated with 500 mgm. of manganese. Much zirconium is also carried down, but never quite completely. Provision is therefore made (in *P. 62*a*) for the detection of these three elements in the pre-

cipitate (if it is large) as well as in the filtrate. If it is not thought necessary to test for zirconium in the precipitate, the certain detection of titanium can be much more quickly accomplished just before precipitating the manganese by diluting the HNO_3 solution, from which the HCl has been removed, with once or twice its volume of water, and adding 3 ccm. 3% H_2O_2 solution. An orange-yellow or orange-red color shows the presence of titanium. (See *P. 65*b*, N. 1.) In the absence of HCl iron does not interfere with this test; nor does even a large quantity of nickel or cobalt prevent a distinct change of color from being seen.

4. In filtering the MnO_2 a cylindrical glass funnel with a small delivery tube is usually employed in quantitative analysis. An ordinary conical funnel is, however, satisfactory, provided the wad of glass wool is made compact and enough asbestos is used. Filtration will, to be sure, be slow if the glass wool is packed very tightly or if the asbestos mat is very thick, but in that case suction may be applied.

5. On evaporating the HNO_3 filtrate titanium and zirconium oxides may separate out, especially if the solution be evaporated almost to dryness. For this reason the solution is evaporated only to about 5 ccm., but even then a small, white precipitate will sometimes be obtained when these elements are present in large amount.

Procedure 62. — Transfer the whole of the $HClO_3$ precipitate (P. 61) if it is small (containing less than 5 mgm. Mn), or 5–10 mgm. of it if it is large, to a casserole; add 1 or 2 grams solid PbO_2, and about 10 ccm. HNO_3 (1.20); boil for about 2 minutes in a casserole covered with a watch-glass; pour the mixture into a test tube, and allow the PbO_2 to settle. (Violet-red solution, presence of MANGANESE.)

If the precipitate is large, dissolve the remainder in hot HCl (1.12) in a casserole, or by pouring a 10–15 ccm. portion repeatedly through the filter, and boil the solution to expel chlorine. To one-tenth of this solution add 5 ccm. KCNS solution. (Deep red color, presence of IRON.) Treat the remainder of the HCl solution by *P. 62*a* to recover any titanium and zirconium that may be present.

Note. — This confirmatory test for manganese is usually superfluous, since the precipitation of MnO_2 by $HClO_3$ is highly characteristic. In order that the PbO_2 test may be satisfactory, the HNO_3 used must be fairly concentrated and the boiling continued for 2 or 3 minutes.

***Procedure 62a.** — To the HCl solution (P. 62), without evaporating it, add NH_4OH (0.96) until the mixture is barely alkaline, avoiding

the addition of more than 2 or 3 drops in excess; heat nearly to boiling for 2 or 3 minutes, filter at once, and wash with hot water. Reject the filtrate. Dissolve the precipitate in a little hot HCl (1.12) (without diluting it with water), reserve it, and unite it with the main HCl solution to be treated in *P. 65*a*.

Note. — In order to avoid as far as possible the precipitation of manganese by NH_4OH, the OH^- concentration is kept small by avoiding an excess of NH_4OH and by having a large quantity of ammonium salt present. Under these conditions the oxidation by the air to the manganic state is slow. If, however, much NH_4OH be added, oxidation takes place rapidly and much manganese may be precipitated as $Mn(OH)_3$, yielding a brown precipitate. Even at best a little manganese will come down, but a moderate amount does not interfere with the subsequent tests for titanium and zirconium.

Procedure 63. — Add about one-tenth of the HNO_3 solution (P. 61) to three or four times its volume of ammonium molybdate reagent, and heat to 60–70°. (Yellow, finely crystalline precipitate, presence of PHOSPHATE.) If there is no precipitate, or only a very small one, treat the remainder of the HNO_3 solution by P. 64; otherwise by P. 65.

Notes. — 1. Phosphate is tested for at this point because a different treatment is necessary when it is present in significant amount, in order to separate from it alkaline-earth elements and to provide for their detection. When phosphate is not present, iron, thallium, titanium, and zirconium can be separated from nickel, cobalt, and the alkaline-earth elements by NH_4OH (as in P. 64); but when considerable phosphate is present the alkaline-earth elements would be partly or wholly precipitated in combination with it. (See P. 51, N. 6.)

2. In order that the phosphate test may be delicate and may appear immediately, a large proportion of the molybdate reagent must be used and the solution must be warmed. The precipitate of ammonium phospho-molybdate is of complicated and somewhat variable composition; it contains ammonium phosphate and molybdic acid, approximately in the proportion $(NH_4)_3PO_4.12MoO_3$.

Procedure 64. — If phosphate is absent, make the HNO_3 solution (P. 62) strongly alkaline with NH_4OH (0.96), using an excess of 3–5 ccm. (Dark red precipitate, presence of IRON.) Filter, and wash the precipitate, using suction if the precipitate is large, and sucking it as dry as possible. Treat the filtrate by P. 66.

Dissolve the precipitate in HCl (1.12), warming if necessary, taking care not to dilute the acid by wash water. To about one-tenth of the solution add 5 ccm. KCNS solution. (Dark red color, presence of IRON.) *Treat the remainder of the solution by *P. 65*a*.

Notes. — 1. If titanium and zirconium are to be tested for, it is important to dissolve the NH_4OH precipitate in HCl of a specific gravity 1.12 (24% HCl) and to avoid dilution, for the separation in *P. 65*a* depends on the concentration of the HCl.

2. The red color obtained on adding KCNS is due to the formation of un-ionized ferric sulphocyanate, $Fe(CNS)_3$. This test may be made in the presence of much HCl; for the acid HCNS is also a highly dissociated acid, which is therefore not displaced from its salt. Much HNO_3 must not, however, be present; for by its action on KCNS, NO_2 may be formed, and this also gives a deep red color with KCNS. This test for iron is an extremely delicate one; and if only a faint color is obtained, the acids used in the process must be tested for iron.

Procedure 65. — When phosphate is present, test one-tenth of the HNO_3 solution (P. 63) for iron, by evaporating it just to dryness, adding 1–2 ccm. HCl (1.20), evaporating again to decompose the HNO_3, diluting to 5 or 10 ccm., and adding 5 ccm. KCNS solution. (Permanent red color, presence of IRON.) To the remainder of the solution add NH_4OH (0.96) until the precipitate formed by the last drop does not redissolve on shaking. If, owing to the addition of too much NH_4OH, the solution becomes alkaline or a large precipitate separates, make it distinctly acid with acetic acid. Add 5 ccm. of a 50% solution of ammonium acetate, and, unless the mixture is already of a brownish red color, add 10% $FeCl_3$ solution, drop by drop, until such a color is produced. Add enough water to make the volume about 100 ccm., boil in a 250 ccm. flask for 5 minutes, adding more water if a very large precipitate separates, and let the mixture stand for a minute or two. Filter while still hot, and wash with hot water. Add 3–5 ccm. more ammonium acetate solution to the filtrate, boil it again, and collect on a separate filter any further precipitate. Make the filtrate alkaline with NH_4OH, adding an excess of 2–3 ccm., filter off and wash any precipitate, uniting it with the main precipitate. (Filtrate, P. 66; precipitate, reject or dissolve in hot HCl (1.12), and treat by *P. 65*a*.)

Notes. — 1. With regard to the test for iron with KCNS and the necessity of removing the HNO_3, see P. 64, N. 2.

2. This method of separation depends on the facts that, upon boiling an acetic acid solution containing much acetate, ferric iron and titanium are completely precipitated, and thallic thallium and zirconium nearly so, in the form of basic acetate or hydroxide; and that all the phosphate present combines with these elements when they are present in excess, and therefore it then passes completely into the precipitate, leaving the bivalent elements in solution. This behavior of the phosphate is due to the fact that the solubility in acids of the phosphates of the trivalent and quadrivalent elements is much smaller than that of the phosphates of the bivalent elements.

3. If upon adding the ammonium acetate the solution becomes of a reddish color, it shows that iron is present in quantity more than sufficient to combine with the phosphate; for a cold solution containing ferric acetate is of a deep red color. If, on the other hand, a colorless solution results (either with or without a precipitate), it shows that there is no excess of iron, and $FeCl_3$ is therefore added, which causes the precipitation of $FePO_4$ as a yellowish white precipitate. Upon boiling, the excess of iron separates completely as a dark red gelatinous precipitate of basic ferric acetate, leaving the supernatant liquid colorless, except when nickel or cobalt is present.

4. The solution is diluted to at least 100 ccm., owing to the large volume of the precipitate, and it must be heated in a capacious flask, owing to its tendency to boil over.

*5. Zirconium may not be completely precipitated under the conditions of this procedure, 1–5 mgm. sometimes remaining in solution, especially when considerable acetic acid is present. To ensure its complete separation, the filtrate is made alkaline with NH_4OH.

*6. The precipitation of thallium in this procedure is not quite complete, but there is no danger of losing even 0.5 mgm. when iron is also present, as is always the case.

***Procedure 65a.** — To the HCl solution (P. 64 or 65, and *62*a*), which should be of a specific gravity of 1.11 to 1.12, add 10–20 ccm. more HCl (1.12), transfer the (cold) solution to a separating funnel, add an equal volume of ether, shake vigorously several times (preferably after inverting the funnel and opening the cock), and then allow the two layers to separate. Draw off the layers separately, and rinse out the funnel with a little ether. Return the aqueous layer to the funnel and treat it with ether as before; if necessary, repeat this treatment once or twice until the ether layer remains colorless. (Water solution, *P. 65*b*; first ether solution, *P. 65*d*; remaining ether solutions, reject.)

Notes. — 1. If the directions are followed, 97–99% of the $FeCl_3$ present passes into the ether layer in each extraction. It is evident from this statement that, even when 500 mgm. of iron are present, substantially all of it will be removed in three extractions. But it is important that the concentration of the HCl solution in contact with the ether layer lie within the narrow limits of 20–22% HCl, corresponding to a specific gravity of 1.10 to 1.11 at 15°. This concentration is realized in the procedure, even though a little stronger acid is used; for some of the HCl passes into the ether layer. The extraction of the $FeCl_3$ is less complete both with stronger and weaker HCl solutions; thus with HCl containing initially either 18 or 25% about 94% of the $FeCl_3$ passes into the ether layer; while with 8% HCl only 4–5% of the $FeCl_3$ is extracted in each shaking. Almost all the thallium, which is present as $TlCl_3$, also passes into the first ether extract.

2. The following are probably the principles involved in this ether extraction. Since iron passes into the ether layer only in the form of $FeCl_3$, the quantity of it extracted by the ether increases, in accordance with the distribution law, the larger the proportion of un-ionized anhydrous $FeCl_3$ in the water layer. This proportion is, however, increased by increasing the concentration of HCl, both in virtue of the reduction of the ionization by the common-ion effect, and of the reduction of the hydrolysis of the ferric salt by the free acid. It is doubtless true that the strong acid has also a dehydrating effect, thereby increasing the anhydrous $FeCl_3$ in the water layer. As the HCl becomes very concentrated, however, another effect, opposite in character, comes into play; namely, ether dissolves in large quantities in the aqueous layer, and HCl and water dissolve in large quantity in the ether layer, thus making the two layers more nearly alike, and doubtless decreasing the distribution-ratio for the $FeCl_3$ between the ether and water layers. With respect to this explanation, it should be added that it is uncertain to what extent complex acids ($HFeCl_4$, etc.) may be involved.

3. Since the color of the ether layer is a sensitive indication of iron, the treatment with ether may be discontinued as soon as a nearly colorless ether extract is obtained. When titanium is present the water layer may remain distinctly yellow, owing to the presence of hydrogen peroxide as impurity in the ether; such a color does not, therefore, show that iron is still present.

4. Titanium and zirconium remain completely in the water layer. When much zirconium is present some of it may be precipitated out as chloride; but this remains suspended in the water layer.

5. Phosphoric acid does not interfere with this separation, and the iron can therefore be extracted even after the basic acetate procedure.

***Procedure 65b.** — Heat the HCl solution (*P. 65*a*) on a water bath until the ether is expelled, add 1 ccm. H_2SO_4 (1.20), evaporate almost to dryness until the H_2SO_4 begins to fume, adding 1 ccm. more H_2SO_4 (1.20) if the residue is solid. If the residue is dark-colored, owing to organic matter, add a few drops HNO_3 (1.42), and evaporate again until the H_2SO_4 begins to fume. Cool, add 5 ccm. water, 10 ccm. 3% H_2O_2 solution, and then 10 ccm. 10% $Na_2HPO_4 12H_2O$ solution. (Orange-yellow to orange-red solution, presence of TITANIUM; white flocculent precipitate, presence of ZIRCONIUM.) Let the mixture stand for at least an hour, filter, and wash the precipitate. (Filtrate, if colored, *P. 65*c*; precipitate, N. 3.)

Notes. — 1. By the addition of H_2O_2 titanium is converted into a sulphate corresponding to the higher oxide, TiO_3, the red color being due to the cathion. This color test is an extremely delicate one, even 0.1 mgm. Ti imparting a distinct yellow color to the solution.

2. By the Na_2HPO_4, zirconium is precipitated as a basic phosphate, $Zr(OH)PO_4$. Its precipitation is slow; but if nothing has separated after half an hour it is safe to conclude that less than 0.5 mgm. zirconium is present, provided care has been taken not to use more H_2SO_4 than is directed in the procedure. If the titanium had not been oxidized by the addition of H_2O_2, it would also give an entirely similar precipitate of $Ti(OH)PO_4$; but from a solution containing H_2O_2 in excess, when titanium is alone present, none of it separates even on standing several hours. When zirconium and titanium are present together, a small proportion of the titanium is carried down with the zirconium and the phosphate precipitate may then have a distinct yellow color.

3. Some of the rare-earth elements, such as thorium, may also be precipitated as phosphate at this point, if these elements have not been proved absent or removed in *P. 52*a*. In such a case the presence of zirconium may be proved by pouring a portion of dilute HF several times through the filter (supported in a celluloid funnel or a platinum ring), evaporating with H_2SO_4 in a platinum dish, diluting, and adding NH_4OH. The rare-earth phosphates would be left undissolved by the HF.

4. Besides titanium and zirconium, the solution from *P. 65*a* will sometimes contain uranium, manganese, and cobalt (carried down in the precipitates in P. 52, *P. 62*a*, and P. 64, respectively); but not in sufficient amount to interfere with the zirconium and titanium tests. The only other element of the aluminum and iron groups that gives a similar color with H_2O_2 in acid solution is vanadium; but this, aside

from the fact that it should not be present, would give no precipitate with Na_2HPO_4 (not even on the addition of Na_2SO_3 in *P. 65*c*).

Procedure 65c. — To the H_2O_2 solution (*P. 65*b*), if colored, add powdered Na_2SO_3, little by little, until the solution is decolorized, and let the mixture stand 20 or 30 minutes. (White flocculent precipitate, presence of TITANIUM.)

Note. — This test serves to confirm the presence of titanium and to enable the quantity of it to be better estimated. H_2O_2 and the sexivalent titanium compound are rapidly reduced by the action of H_2SO_3, even in the cold, and titanium then precipitates as $Ti(OH)PO_4$. As in the case of zirconium, the precipitation takes place slowly. When there is only a faint color with H_2O_2, no precipitate will be obtained; but 0.5 mgm. of titanium is easily detected if the concentration of the sulphuric acid does not exceed 1 ccm. H_2SO_4 (1.20) in 25 ccm. solution.

Procedure 65d. — Evaporate the first ether extract (*P. 65*a*) in a casserole, and dissolve the residue in 3–5 ccm. H_2SO_4 (1.20) and 3–5 ccm. water. To the cold solution in a test tube add 2–3 ccm. 1% KI solution and powdered Na_2SO_3, a little at a time, until the iodine color has permanently disappeared. (Yellow precipitate, presence of THALLIUM.) Filter, using preferably a hardened filter when the precipitate is small. Collect a little of the precipitate on a clean platinum wire and introduce the wire into a colorless gas flame. (Momentary green flame, presence of THALLIUM.)

Notes. — 1. The precipitation of thallium as TlI is practically complete, provided that the volume of the solution is small, say less than 15 ccm. The presence of iron does not prevent a good blank being obtained, nor does its presence in large quantity (500 mgm.) prevent the detection of 0.5 mgm. of thallium. TlI is readily oxidized to the soluble TlI_3 by iodine; therefore an excess of sulphite must be present.

2. Any quantity of thallium in excess of 10–15 mgm. is precipitated in P. 11, except when the solution there treated with HCl contains the thallium in the thallic state.

3. The green flame test is very delicate and characteristic, but on account of the volatility of the thallium compound the green color is seen only at the moment in which the wire is introduced into the flame. A hardened filter is recommended when the precipitate is small, because the precipitate can be more readily collected on the wire on account of the smooth surface of the filter.

Procedure 66. — Into the ammoniacal solution (P. 64 or P. 65) pass H_2S gas until the mixture after shaking blackens lead acetate paper held above it. (Black precipitate, presence of NICKEL or COBALT.) Filter, and wash the precipitate with water containing a very little $(NH_4)_2S$. (Precipitate, P. 67; filtrate, P. 81.)

Notes. — 1. In precipitating NiS, the use of H_2S has the advantage that the nickel is all thrown down at once, while with $(NH_4)_2S$ some of it usually remains in the solution, giving it a dark brown color. If found more convenient, $(NH_4)_2S$ can of course be used, the filtrate being boiled to throw down the unprecipitated nickel, as described in P. 51.

2. The filtrate is in general tested for the alkaline-earth elements; for these may be precipitated with the aluminum and iron groups when phosphate or certain other acid radicals are present, as discussed in P. 51, N. 6 and 7.

Procedure 67. — Transfer the H_2S precipitate (P. 66) with the filter to a casserole, and add 10–30 ccm. of a cold mixture of 1 volume HCl (1.12) and 5 volumes of water. Digest in the cold for 5 minutes, stirring the mixture frequently, and filter. Treat the residue by P. 68.

Boil the HCl solution until the H_2S is completely expelled, add 10% NaOH solution until the mixture is slightly alkaline, transfer to a casserole, cool, and add 0.5–1 gram Na_2O_2, a small portion at a time. Boil for several minutes to decompose the excess of Na_2O_2 and cool the mixture; filter off the precipitate, and treat it by P. 68, uniting it with the residue already obtained in the HCl treatment. Make the solution acid with acetic acid, warm it to about 60°, and pass in H_2S for 2 or 3 minutes. (White flocculent precipitate, presence of ZINC.) Apply to the precipitate the confirmatory test as described in P. 57.

Notes. — 1. This treatment with dilute HCl serves to extract almost completely the zinc which may be present in this precipitate, owing to its having been carried down in the Na_2O_2 precipitate as described in P. 52, N. 11. A small proportion of the nickel and cobalt present (5–20%) always dissolves in the dilute HCl, and the subsequent treatment with Na_2O_2 serves to separate them from the zinc. This separation is satisfactory when, as in this case, the nickel and cobalt are present in such small quantity that only an insignificant amount of zinc is carried down with them. When, therefore, the H_2S precipitate is small, it may, instead of being treated with dilute HCl, be dissolved

at once in *aqua regia* and the solution treated directly as described in the last paragraph of the procedure.

2. This procedure must always be followed in order to determine whether or not zinc is present in the substance, except in the case that a satisfactory test for it has already been obtained in P. 57, or in the case that the original Na_2O_2 precipitate (P. 52) was small.

Procedure 68. — Transfer the residue insoluble in dilute HCl, and the Na_2O_2 precipitate (P. 67), with the filters to a casserole, add 5–15 ccm. HCl (1.12) and a few drops HNO_3 (1.42), warm until the black precipitate is dissolved, and filter off the paper. Evaporate the solution nearly to dryness to expel most of the acid, add about 5 ccm. water, and then NaOH solution, drop by drop, until the mixture is neutral, or until a permanent precipitate just forms. Test one-half of this mixture for cobalt by P. 69, and the remainder for nickel by P. 70.

Procedure 69. — To one-half of the neutral solution (P. 68) add 15 ccm. 30% acetic acid, and then 50 ccm. 30% KNO_2 solution; dilute to 100 ccm., and allow the mixture to stand at least half an hour if no precipitate forms sooner. (Yellow, finely divided precipitate, presence of COBALT.) Filter, and wash with KNO_2 solution. If the precipitate is very small, incinerate the filter. Introduce a portion of the precipitate, or of the ash, into a borax bead made in the loop of a platinum wire, and heat strongly, adding more of the precipitate or ash if no color is obtained. (Deep blue color, presence of COBALT.)

Notes. — 1. The yellow precipitate is potassium cobalti-nitrite, $K_3Co(NO_2)_6$, which in solution dissociates into K^+ and the complex anion $Co(NO_2)_6^{\equiv}$. The precipitate is somewhat soluble in water, but very difficultly soluble in a concentrated KNO_2 solution, owing to the common-ion effect of the potassium-ion. In the formation of this substance the cobaltous salt is oxidized to the cobaltic state by the nitrous acid displaced from its salt by the acetic acid, the cobaltic salt combining as fast as formed with the potassium nitrite, according to the equations:

$$Co^{++}(NO_2^-)_2 + 2HNO_2 = Co^{+++}(NO_2^-)_3 + H_2O + NO \text{ and}$$
$$Co^{+++}(NO_2^-)_3 + 3K^+NO_2^- = K_3Co(NO_2)_6.$$

2. The formation of the $K_3Co(NO_2)_6$ precipitate takes place slowly, but even when very little cobalt is present (0.1–0.2 mgm.) a distinct test is obtained within 10 minutes; but the complete precipitation of a large amount of cobalt requires several hours, so that the method is

ill adapted for the removal of cobalt before testing for nickel. Moreover, when nickel is present, some of it is carried down with the cobalt, and this is true even when the total amount of nickel is small. For these reasons the test for nickel is made in a separate portion.

3. Nickelous salts are not oxidized by nitrous acid, and are not precipitated by KNO_2 except in a very concentrated solution, when a dark yellow to dark red precipitate of potassium nickelous nitrite, $K_4Ni(NO_2)_6$, may separate. By making the volume large, as directed in the procedure, there is no danger of the precipitation of nickel.

Procedure 70. — To the remainder of the neutral solution (P. 68) add 10% KCN solution, a few drops at a time, until all or nearly all of any precipitate that may form at first redissolves; then add 0.5–3 ccm. more (according to the amount of the KCN precipitate). Heat to 50 or 60° in an open casserole, with frequent stirring, for 5 minutes, or longer if the solution has not become light-colored. Filter off and reject any small precipitate that may remain. To the filtrate, preferably in a test tube, add freshly prepared, concentrated NaBrO solution (see N. 3) until a piece of filter paper moistened with KI and starch solutions, when dipped into the solution, is colored blue or brown. Allow the mixture to stand 5–10 minutes, and filter. (Brown to black precipitate, presence of NICKEL.)

Wash the precipitate; dissolve it, or a small portion of it if it is large, in 2–3 ccm. HNO_3 (1.20); add 3–5 ccm. 10% tartaric acid solution, neutralize with 10% NaOH solution, and add 3 or 4 ccm. in excess. Pass in H_2S for about 1 minute, filter out any precipitate that may form, and saturate the filtrate with H_2S. Filter again if there is a precipitate. (Brown coloration, presence of NICKEL.)

Notes. — 1. The reactions involved in the first test for nickel are as follows: When a little KCN is added to the neutral solution, precipitates of (green) $Ni(CN)_2$ and (dark brown) $Co(CN)_2$ result, except when only small amounts of these elements are present. The addition of more KCN causes the precipitate to dissolve, owing to the formation of soluble complex cyanides, as $K_2^+[Ni(CN)_4]^=$ and $K_4^+[Co(CN)_6]^{==}$. The complex nickel salt is stable in the air, but that of cobalt salt is very readily oxidized according to the equation:

$$\underset{\text{(Potassium cobalto-cyanide.)}}{2K_4^+[Co(CN)_6]^{==}} + O + H_2O = \underset{\text{(Potassium cobalti-cyanide.)}}{2K_3^+[Co(CN)_6]^{=}} + 2K^+OH^-.$$

The first action of the NaBrO is to decompose the excess of KCN, chiefly with formation of KCNO. It then oxidizes the nickel to the nickelic state, which is then immediately precipitated as brownish black $Ni(OH)_3$ by the NaOH present. The cobalt, though already in the cobaltic state, is not precipitated as $Co(OH)_3$, because the complex ion, $[Co(CN)_6]^{=}$, is so slightly ionized into its constituent-ions (Co^{+++} and $6CN^-$) that the concentration of the Co^{+++} does not suffice to produce with the OH^- present the solubility-product for the $Co(OH)_3$, and that of the CN^- is so small that it is only very slowly oxidized by the NaBrO.

2. In executing this procedure the following precautions should be observed: A very large excess of the strong KCN solution over that required to redissolve the precipitate should not be added, for the excess must be destroyed by the NaBrO before the nickel can be oxidized and precipitated by it. Yet there must be sufficient KCN added, not only to combine with all the cobalt, but to furnish a moderate excess in order that the oxidation to the cobalti-cyanide may take place rapidly. Care must also be taken to heat the solution long enough in the air to complete this oxidation before the NaBrO is added; for otherwise the latter reagent after destroying the free KCN will oxidize the decomposable cobalto-cyanide with precipitation of $Co(OH)_3$, just as it does the nickelo-cyanide. The completion of the oxidation by the air is indicated by the disappearance of the dark color in the solution. Finally, one must make sure (by applying the iodide-starch test) that an excess of NaBrO over that required to oxidize both the cyanide and the nickel has been added. If these precautions are observed, there is no difficulty in securing a precipitate with 0.2 mgm. of nickel nor in causing 300 mgm. of cobalt to remain entirely in solution.

3. The hypobromite reagent is prepared by adding liquid bromine to a known volume of 10% NaOH solution until the solution becomes distinctly red, owing to the presence of excess of bromine; and then adding half as much more NaOH solution. This solution may be filtered through a hardened filter. It decomposes fairly rapidly, with formation of bromate and bromide, and also with evolution of oxygen, and should therefore not be used when more than a few days old. Instead of this reagent, bromine water and NaOH solution may of course be used. The concentrated hypobromite solution is recommended because a much smaller volume of it is required to decompose the large excess of cyanide used in the procedure.

4. When an alkaline tartrate solution containing a small amount of nickel (even 0.1–0.2 mgm. in 20 ccm.) is saturated with H_2S a clear brown solution is obtained. With somewhat larger amounts of nickel

(10–20 mgm.) the liquid is opaque, but runs through a filter very readily. The condition of the nickel in this solution is not known. The presence of the tartrate serves merely to prevent the precipitation of $Ni(OH)_2$ by the NaOH solution, owing to the formation of a complex salt containing the nickel in the anion. The brown color does not appear until the alkaline solution is nearly saturated with H_2S, so that care must be taken to use an excess of H_2S.

5. This confirmatory test for nickel is not interfered with by moderate amounts of other elements of this group, such as cobalt and iron (which, however, should not be present at this point), for on leading H_2S into an alkaline tartrate solution containing these elements, they are completely precipitated as sulphides and may be filtered off, yielding a filtrate which in the absence of nickel remains clear when saturated with H_2S, or becomes dark brown when it is present in even small amounts.

Test Analyses

Numerous analyses were made to test the efficiency of the process described above. Nearly all of those which were made after the procedure assumed final form are reproduced in the tables below. Almost all the analyses relating to the common elements alone were made before the procedures for the rare elements had been worked out, but the process for the analysis of mixtures containing only the common elements was at that time substantially the same as given above. In these tables the numbers in each vertical column show the weights in milligrams of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable, and therefore conclusive; and when the element was absent, that a good blank test was obtained. When the test was very small, especially in comparison to the quantity of the element present, though still unmistakable, this is sometimes indicated by the symbol S—. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing to the appearance or small size of the precipitate, this is indicated by the letter D. When the test was not tried, if the element was present, a dash is used in place of a letter; or, if the element was not present, dots are inserted.

Common Elements

The following analyses (Nos. 114–119) were begun at P. 51; P. 61 was introduced before P. 52.

T. A. No.	114	115	116	117	118	119
Mn	10 S	2 S	1 S	500 S	500 S	0 S[4]
Al	10 S	2 S	1 D[1]	0 D[1]	2 S	0 D[1]
Cr	10 S	2 S	1 S	0 S	2 F[8]	0 S
Zn	10 S	2 S	1 S	0 S	2 S	0 S
Fe	10 S	2 S	1 S	0 S	2 S	500 S
Ni	10 S	2 S	1 S	0 S	2 S	0 S
Co	10 S	2 S	1 S	0 S	. .	0 S

Analyses 120–125 were begun at P. 61.

T. A. No.	120	121	122	123	124	125
Mn	500 S	500 S	100 S	1 S	. .	. .
Fe	0 S	1 S—	1 S	100 S	500 S	500 S
Ni	2 S	1 S	. .	. .	3 S	1 S—

Analyses 126–127 were made by P. 69; analyses 128–130 by P. 70.

T. A. No.	126	127	128	129	130
Co	0 S	0.5 S	150—	150—	150—
Ni	250—	250—	0 S	0.3 S	0.15 S

The following analyses (Nos. 131–143) were begun at P. 52.

T. A. No.	131	132	133	134	135	136
Al	0 S[2]	0 S[2]	0 S[2]	0 S[2]	0 S[2]	0 S[2]
Cr	2 S	1 S	0 S	. .	0 S	1 S
Zn in P. 57 .	2 F	4 F	10 F	20 S—[5]	5 F	0 S
Zn in P. 67 .	2 S	4 S	10 S	20 S	5 S	0 S
Mn	500 S	500 S	500 S	500 S	0 S	2 S
Fe	0 S	0 S	0 S	0 S	500 S	500 S
Ni	0 S	0 S	0 S	0 S	0 S	2 S

T. A. No.	137	138	139	140	141	142	143
PO_4	. .	. .	. .	. .	. .	200 S	200 S
Zn in P. 57	5 F	5 S—[7]	10 S—[6]	3 F	5 S—[5]	5 F—[8]	10 F[8]
Zn in P. 67	5 S	5 S	10 S	3 —	5 —	5 —	10 S
Fe	500 S	500 S	500 S	. .	. .	. .	. .
Ni	. .	. .	. .	250 —	250 —	250 —	250 S
Co	. .	. .	. .	250 —	250 —	250 —	250 S

The following analyses (Nos. 144–155) were begun at P. 52; P. 61 was omitted.

T. A. No.	144	145	146	147	148	149
Al	0 S[2]	3 S	3 S	0 S[2]	0 S[2]	0 S[2]
Cr	0 S	2 S	1 S	1 S	0 S	10 S
Zn in P. 57	0 S	5 S—[5]	3 F	3 S—	3 F	20 S—[5]
Zn in P. 67	0 S	5 S	3 S	3 S	3 S	20 S
PO_4	0 S	200 S	200 S	100 S	100 S	100 S
Fe	500 S	500 S	500 S	100 S	100 S	100 S
Ni	0 S	2 S	1 S	0 S	. .	. .
Co	0 S	2 S	1 S	0 S	100 S	100 S
Ba	0 S	2 S	1 S—	0 S	0 S	0 S
Ca	0 F[9]	0 F[9]	0 F[9]	4 S	0 F[9]	100 S
Mg	0 S	2 S	1 S	2 S	2 S	100 S

T. A. No.	150	151	152	153	154	155
Cr	2 S	. .	0 S	. .	2 S	1 S[10]
Zn in P. 57	3 F	5 S	0 S	1 F	. .	. .
Zn in P. 67	3 —	5 S	0 S	1 S	. .	. .
PO_4	100 S	100 S	. .	. .	. .	. .
Fe	100 S	100 S	0 S	. .	. .	. .
Co	100 S	100 S	500 S	500 S	. .	. .
Ba	2 S	1 F	. .	. .	100 S	100 S

Mixtures Containing the Rarer Elements

Analyses 156–161 were begun at *P. 58*a*.

T. A. No.	156	157	158	159	160	161
Cr	0 S	0 S	2 S	1 S[11]	. .	. .
U	100 S	0 S	100 S	100 S	100 S	1 S
V	0 S	100 S	100 —	100 —	1 S	100 S

Analyses 162–165 were begun at *P. 58*f*.

T. A. No.	162	163	164	165
Al	500 S	500 S	1 S	1 S
Be	0 S	2 S[12]	0 S	100 S

Analyses 166–170 were begun at *P. 58*a*.

T. A. No.	166	167	168	168*a*	169	170
Zn	. .	. .	. .	. .	200 —	200 S
Al	200 —	200 —	. .	. .	. .	200 S
Be	. .	. .	50	50 S	. .	. .
U in *P. 58*c* and *d*	2 F	3 S—	2 F	2 S—	2 S	2 F
U in *P. 58*h* . . .	2 —	3 —	2 —	2 S—	2 S—	2 S

Analyses 171–176 were begun at P. 64; analysis 176 at P. 52.

T. A. No.	171	172	173	174	175	176
Al	. .	. .	. .	. .	. .	200 —
Mn	. .	. .	. .	. .	. .	200 S
Fe	500 S	500 S	0.5 S	500 S	500 S	200 S
Ti	0 S	1 S	5 S	. .	. .	. .
Zr	0 S	1 S	. .	. .	. .	. .
Tl	0 S	. .	. .	1 S	0.5 S	1 S[13]

The following analyses (Nos. 177–181) were made by Mr. R. D. Gale, who had had no previous experience in connection with the process. The first analysis was with a known mixture, the remaining four were with unknowns. Mr. Gale received no assistance while making an analysis (except in T. A. No. 179), but all the precipitates and solutions were preserved in order that the causes of mistakes might afterwards be investigated. The process was practically in its final form with exception of the procedures relating to the separation of chromium, uranium, and vanadium (*P. 58*b* to *e*), which were revised on account of the results of these analyses; moreover, uranium was not tested for in *P. 58*h*. Test Analyses 156–161 were made at a later date to test these procedures in their final form.

T. A. No.	177	178	179	180	181
Begun at	P. 52	P. 51	P. 51	P. 52	P. 51
Cr	2 S	1 S— [15]	1 S	1 S	2 F [14]
U	3 S	1 F [16]	1 F [16]	0 S	100 S
V	3 S	1 S	1 S	0 S	100 S [21]
Zn in P. 57	3 S	1 F	1 S	1 F	100 S [22]
Zn in P. 67	3 D	1 S—	1 . .	1 S—	100 S
Al	3 S	200 S	1 S [17]	0 S	0 S
Be	3 S	1 S	0.5 S	0 S	0 S
Mn	3 S	1 S	1 S	200 S	300 S
PO_4	. .	. .	. .	320 S	. .
Fe	3 S	200 S	1 S	1 S [18]	1 S [19]
Ti	3 S	1 S	0.5 S	1 S	0 S
Zr	3 S	1 S—	1 S	1 F [23]	0 S
Ni	3 S— [20]	1 S	1 S	200 S	1 F
Co	3 S— [20]	200 S	1 S	1 S	1 S
Ca	. .	. .	. .	200 S	. .
Ba	. .	. .	. .	2 S	. .

NOTES

[1] The presence of aluminum in the reagents made the result doubtful.

[2] A distinct precipitate of $Al(OH)_3$ was obtained in P. 53, but not more than with the reagents alone.

[3] Excess of HCl was added in P. 53 and the solution boiled, as a result of which the chromic acid was reduced. On analyzing another mixture, and using HNO_3, a satisfactory test for chromium was obtained.

[4] The absence of manganese was confirmed by fusing some of the iron salt on platinum foil with Na_2CO_3 and KNO_3: no green color was obtained.

[5] A small precipitate of ZnS was obtained in P. 57, which did not contain more than 1 mgm. Zn. See C. E., P. 52, N. 11.

[6] A small precipitate of ZnS was obtained in P. 57, corresponding to 2 or 3 mgm. Zn.

[7] In this analysis a large excess of alkali was added before the Na_2O_2 in P. 52, and the mixture was well stirred.

[8] This analysis was repeated, except that the acid solution in P. 52 was poured slowly into an excess of hot alkali before adding Na_2O_2: a distinct test for zinc was then obtained in P. 57.

[9] A distinct test for calcium was obtained (except possibly in T. A. No. 148); the iron salt was found to contain about 2 mgm. Ca with 500 mgm. Fe.

[10] This analysis was repeated, except that no Na_2CO_3 was added in P. 52: the test for chromium failed.

[11] See C. E., *P. 58*b*, N. 2.

[12] The precipitate of $Be(OH)_2$ obtained in *P. 58*k* was large and corresponded to 2 mgm. Be, thus showing that much smaller amounts could be easily detected.

[13] The basic acetate procedure (P. 65) was used instead of P. 64: good tests for thallium were obtained both in the precipitate and in the filtrate. Compare C. E., P. 65, N. 6.

[14] Chromium was lost in *P. 58*a*, owing to the presence of H_2O_2 (from the peruranate, see C. E., P. 52, N. 6 and *P. 58*b*, N. 2) and the addition of a large excess of acid.

[15] A slight blue coloration was obtained with H_2O_2 in *P. 58*b*, corresponding to not more than 0.5 mgm. Cr. No lead nitrate was added.

[16] The directions in *P. 58*c* were faulty; too little phosphate was added to precipitate 1 mgm. U.

[17] A good test for aluminum was obtained in *P. 58*g*, but the confirmatory test (P. 54) failed.

[18] The test for iron in P. 65 was a failure; the iron was found with the manganese in P. 62.

[19] Satisfactory tests for iron were obtained in P. 62 and in P. 64.

[20] $(NH_4)_2S$ was used instead of H_2S in precipitating the sulphides in P. 66, and some nickel was lost in the brown solution. Nickel and cobalt were also lost in P. 67 in the treatment with dilute HCl, owing to the rejection of the Na_2O_2 precipitate.

[21] Only a few milligrams of vanadium were found in filtrate from P. 51.

[22] About twice as much zinc was found in P. 57 as in P. 67.

[23] Owing to the insolubility of $Zr(OH)PO_4$ it is scarcely possible for zirconium and phosphate to occur together in the analysis of the aluminum and iron groups. The zirconium was undoubtedly lost in dissolving the precipitates obtained in P. 52–65.

Although all possible combinations of small and large quantities of the elements have not been investigated, the test analyses are sufficiently varied to justify general conclusions as to the reliability of the method of separation and detection of the elements.

solution was evaporated to about 40 ccm. and made alkaline with NH_4OH: a dirty gray precipitate separated.—50 mgm. V as Na_3VO_4 were boiled with HCl (1.20) to reduce the vanadium; the mixture was diluted to 100 ccm. and made alkaline with NH_4OH: a small gray precipitate, with a greenish shade, separated. Several ccm. NH_4OH were added: the precipitate dissolved.

Precipitation of Vanadium in P. 51 or by Ammonium Hydroxide alone when Iron or Zinc is Present.—500 mgm. Fe as $FeSO_4$ and 100 mgm. V as Na_3VO_4 were treated with H_2S by P. 21, evaporated to 40 ccm. and treated by P. 51; the filtrate was tested for vanadium by *P. 51*a*: less than 1 mgm. V was found.—The experiment was repeated with 500 mgm. Fe and 10 mgm. V: no vanadium was found in the filtrate.

500 mgm. Fe as $FeCl_3$ and 100 mgm. V as Na_3VO_4 were dissolved in 40 ccm. containing 4 ccm. HCl (1.12); the solution was made alkaline with NH_4OH, and (without adding $(NH_4)_2S$) the mixture was filtered; the filtrate was tested for vanadium by *P. 51*a*: only a trace of vanadium was found.—The experiment was repeated with 500 mgm. Fe as $FeSO_4$ and 100 mgm. V as Na_3VO_4: the mixture was allowed to stand and shaken frequently in order that the iron might be completely precipitated: no vanadium was found in the filtrate. 50 mgm. Fe as $FeCl_3$ and 15 mgm. V as hypovanadic acid and several grams NH_4Cl were dissolved in a little HCl and 100 ccm. water; the solution was made alkaline with NH_4OH, and the filtrate was evaporated to dryness, ignited, dissolved in a little HCl and tested for vanadium by *P. 51*a*: only a trace of vanadium was found. Therefore, vanadium is almost completely carried down when a three to fivefold excess of iron is present.

300 mgm. Zn as $ZnCl_2$ and 10 mgm. V as H_3VO_4 were treated with H_2S by P. 21, evaporated to 30 ccm. and treated by P. 51; the filtrate was tested for vanadium by *P. 51*a*: 3 or 4 mgm. V were found. The ZnS precipitate was analyzed by the regular procedure: the remainder of the vanadium was found.

Reduction of Vanadic Acid by HI and its Subsequent Behavior with the Group Reagents.—According to Gooch and Curtis (*Am. J. Sci.* [4] 17, 45. 1904), the first stage of the reduction, that to V_2O_4, takes place rapidly in a dilute HI solution, but the second stage, that to V_2O_3, takes place slowly and only in hot concentrated solutions. When a mixture containing 60 mgm. V_2O_3, 1 gram KI and an excess of HCl was evaporated to 2 ccm., about 97% of the vanadium was reduced to a salt corresponding to V_2O_3.

In our experiments 1 mgm. V as Na_3VO_4 was dissolved in 15 ccm. HCl (1.20) in a 50 ccm. round-bottomed flask; 1 gram NH_4I was added, and the mixture was evaporated carefully to 2 or 3 ccm.; a capillary ebullator tube being used to prevent bumping. The mixture was diluted with 10 ccm.

water, and NH_4OH (0.96) was added until the solution after shaking smelled distinctly of it: a dark green precipitate formed. A few drops of colorless ammonium sulphide were added: the precipitate did not dissolve. It was filtered off and dissolved in a little HNO_3; a large excess (5 to 10 ccm.) of NH_4OH (0.90) was added and the mixture saturated with H_2S: the solution became red, showing the presence of vanadium. The filtrate from the NH_4OH precipitate was tested for vanadium in the same way: only a very small amount was found.—The experiment was repeated, except that the evaporated mixture was diluted to 20 ccm.: more vanadium was found in the filtrate than in the precipitate.—The experiment was repeated, the mixture being diluted to 40 ccm.: all the vanadium was found in the filtrate.

The experiment was repeated several times with 100 mgm. V, the mixture being diluted to 20 ccm. after the evaporation: on adding NH_4OH a dark brown precipitate separated, but it dissolved completely or in large part on adding a few drops of colorless $(NH_4)_2S$.

The experiment was repeated with 50 mgm. V; after the first evaporation 15 ccm. HCl (1.20) and 1 gram NH_4I were added, and the evaporation repeated; the mixture was diluted to 50 ccm.: a large, dark greenish-colored precipitate separated on the addition of NH_4OH, and it did not dissolve on adding several drops $(NH_4)_2S$. The filtrate was evaporated nearly to dryness; an excess of 5 ccm. NH_4OH (0.90) was added, and the mixture saturated with H_2S: not more than 0.5 mgm. V was found in the filtrate. The last experiment was repeated with 5 and with 10 mgm. V: in the experiment with 5 mgm. only a very slight precipitate was obtained on adding NH_4OH, and it quickly redissolved. With 10 mgm. a precipitate was obtained, but about half the vanadium was found in the filtrate. Therefore in a volume of 50 ccm. the precipitation is fairly satisfactory for large amounts of vanadium but not for small amounts. The above results were not perfectly reproducible, but each of them was obtained several times.

A number of attempts were made to reduce 50 to 100 mgm. V as Na_3VO_4 by evaporating as described above with 10 to 15 ccm. pure concentrated HI, and to precipitate the vanadium with NH_4OH after diluting to 40 or 50 ccm.; but the precipitation was much less complete than after the reduction with NH_4I and HCl, probably owing to the larger proportion of iodine that was found to be retained in the solution in the former case. The experiments were repeated with HI that had been exposed to the air and contained much iodine: the precipitation was still less complete.

Rate of Oxidation of Trivalent Vanadium in the Presence of NH_4OH, and of $(NH_4)_2S$.—50 mgm. V were reduced twice by evaporation with 15 ccm. HCl (1.20) and 1 gram NH_4I to 2 or 3 ccm.; the residue was

diluted to 50 ccm., and made alkaline with NH_4OH. The mixture was divided into two parts; one was filtered at once and the second after half an hour; both filtrates were tested for vanadium by *P. 51*a*: a very poor test was obtained in the first filtrate, and a good one in the second.—The experiment was repeated, except that the second portion was filtered after 2 hours: the first filtrate gave a slight test for vanadium; the second contained 2–4 mgm. V. Therefore the oxidation takes place slowly in the presence of NH_4OH.

The experiments were repeated except that several drops colorless $(NH_4)_2S$ were also added: the filtrates, obtained at once, after half an hour, and after 2 hours gave only slight tests for vanadium. Therefore the addition of a little $(NH_4)_2S$ does not cause the vanadium hydroxide to dissolve, and the rate of oxidation is slower in the presence of $(NH_4)_2S$ than in that of NH_4OH alone.

The oxidation, by the oxygen of the air, of the trivalent vanadium after dilution is therefore much too slow to account for the abnormal results, such as the nearly complete precipitation of 50–100 mgm. V in one experiment, and the non-precipitation in another performed under apparently the same conditions.

G. D., § 2: Action of HCl on NiS or CoS.—Herz (*Z. anorg. Chem.*, **27**, 390, and **28**, 343. 1901) treated sulphides, which had been kept on filters for several days after precipitation, with 0.5 normal HCl (1 volume HCl [1.12] and 12 volumes water), and found that the evolution of H_2S could not be detected by odor or by action on paper moistened with a lead salt. On the other hand, he found H_2S to be evolved fairly rapidly by the action of 0.5 normal HCl on freshly precipitated sulphides. He concludes that there are two allotropic forms of the sulphides, one that is soluble in 0.5 normal HCl and one that is not. As Glixelli (*Z. anorg. Chem.*, **55**, 297. 1907) has pointed out, this evidence of decreased solubility is not conclusive; for the rate of reaction with the old sulphides may simply be much slower. The following experiments show that NiS, at any rate while freshly precipitated, is not a mixture of two sulphides differing markedly in solubility.

200 mgm. Ni as NiS, precipitated in the cold by passing H_2S into NH_4OH solution, were digested in the cold for a known time with about 30 ccm. dilute HCl (1 volume HCl [1.12] and 5 volumes water). The HCl was first saturated with H_2S, and H_2S was passed through the mixture in a small flask during the treatment. The mixture was filtered, and the experiment repeated several times with the NiS residue. The amount of nickel dissolved in each treatment was estimated by adding NH_4OH and precipitating the nickel as NiS by passing in H_2S: in the first treatment of 15 minutes, about 20 mgm. Ni dissolved; in each of the next four

treatments of 15 minutes each, steadily decreasing amounts of Ni dissolved; and in the fifth treatment the amount was estimated to be 10 mgm. Ni. The sixth and seventh treatments were each for half an hour: somewhat more nickel dissolved than in the fifth treatment for 15 minutes. The eighth treatment was for 4 hours: nearly as much dissolved as in the first treatment (say 18 mgm.). Over night, without passing the current of H_2S, about 20 mgm. Ni dissolved. In a last treatment for 6 hours, 25 or 30 mgm. dissolved. The final residue contained only about 30 mgm. Ni.—A similar series of experiments was performed, except that the HCl was not saturated with H_2S and no H_2S was passed through the mixture: the results were similar, except that the NiS dissolved more slowly, owing to the fact that the mixture was very little stirred.

100 mgm. Ni as NiS (precipitated by H_2S in NH_4OH solution) were digested with 30 ccm. dilute HCl (1 volume HCl [1.12] and 3 volumes of water) for 5 minutes: about 5 mgm. Ni dissolved.—The experiment was repeated with HCl (1.12): the amount of Ni that dissolved was not much greater than in the preceding experiment.—The last experiment was repeated with 1 mgm. Ni: only a small proportion of the nickel dissolved.

Action of HCl on NiS when Other Sulphides Are also Present.—500 mgm. Fe as $FeSO_4$ and 5 mgm. Ni as $NiSO_4$ were dissolved in 50 ccm. water containing 2 ccm. H_2SO_4 (1.84), and the solution treated at about 40° with NH_4OH and $(NH_4)_2S$, as described in P. 51: the filtrate was clear and light-colored, showing that it contained no nickel. The precipitate was dried by suction, and treated in a casserole with 30 ccm. cold dilute HCl (1 volume HCl [1.12] and 5 volumes water), with frequent stirring, for 5 minutes: only a very small black residue remained, which was found to contain about 0.5 mgm. Fe, but no nickel.—The experiment was repeated, except that ferric chloride was used instead of ferrous sulphate: the residue contained 1 or 2 mgm. Fe and a mere trace of nickel.—Both experiments were repeated, except that the sulphides were precipitated at about 90° by passing H_2S into NH_4OH solutions. In the experiment with ferrous iron the residue insoluble in dilute HCl contained nearly 1 mgm. Fe and less than 1 mgm. Ni; in the experiment with ferric iron the residue contained about 1 mgm. Fe and nearly all the nickel.—The last experiment was repeated with 500 mgm. Fe as $FeCl_3$ and 2 mgm. Ni as $NiSO_4$: the residue insoluble in cold dilute HCl contained a little iron and nearly all the nickel.—The first of the above experiments was repeated with 500 mgm. Fe as $FeSO_4$ and 10 mgm. Ni as $NiSO_4$; the residue insoluble in dilute HCl and also the filtrate were tested for iron and nickel: the residue contained about 1 mgm. Fe and 5 mgm. Ni; the HCl solution contained also about 5 mgm. Ni.—The experiment was repeated, except that the sulphides were precipitated at about 90° by passing H_2S into an NH_4OH solution:

the residue insoluble in dilute HCl contained about 0.5 mgm. Fe and 3 or 4 mgm. Ni.

500 mgm. Mn as $MnSO_4$ and 5 mgm. Ni as $NiSO_4$ were dissolved in 2 ccm. H_2SO_4 (1.84) and 50 ccm. water, and the solution was treated with NH_4OH and $(NH_4)_2S$, as described in P. 51; the filtrate was clear, showing the absence of nickel. The precipitate was digested with 30 ccm. cold dilute HCl (1 volume HCl [1.12] and 5 volumes water), with frequent stirring, for 5 minutes: the small, dark-colored residue on analysis was estimated to contain 3 or 4 mgm. Ni: the HCl solution contained only about 0.5 mgm. Ni.

The experiment was repeated with 500 mgm. Zn as $ZnSO_4$ and 2 mgm. Ni as $NiSO_4$: after 10 minutes' treatment with the dilute HCl, a very large residue remained; the HCl solution contained only about 100 mgm. Zn and no Ni. The second treatment with HCl lasted over night: about 300 mgm. Zn and no Ni dissolved. The third treatment lasted 2 days: the residue was small and dark-colored and contained over 1 mgm. Ni and little or no Zn; the HCl solution contained about 100 mgm. Zn and a little Ni.—The experiment was repeated with HCl (1.12): a black residue remained.

These experiments show that small amounts of NiS may be dissolved completely when distributed throughout a large precipitate of iron sulphide, but that they are not readily dissolved in the presence of ZnS or MnS. They also show that ZnS dissolves slowly in dilute HCl, just as NiS does.

G. D., § 6: Precipitation of Vanadium by Alkaline Hydroxides when Uranium Is Present.—For the insolubility of uranyl vanadate, see v. Klecki, *Z. anorg. Chem.*, **5**, 381 (1894); Carnot, *Compt. rend.*, **104**, 1850 (1887); also C. E., *P. 58*a*, N. 3.

50 mgm. V as Na_3VO_4 and about 250 mgm. U as $UO_2(NO_3)_2$ were dissolved in 3 or 4 ccm. HNO_3 (1.20) and 30 ccm. water; the solution was made alkaline with NH_4OH (0.96): a large yellow precipitate separated. This was filtered off and the solution was tested for vanadium by *P. 58*e*: not more than 1 mgm. was found. In this experiment there was just sufficient uranium to form $UO_2NH_4VO_4$.—The precipitate obtained in the preceding experiment was dissolved in a little HNO_3, diluted to about 15 ccm., and poured into about 20 ccm. 10% NaOH solution: a large yellow precipitate separated. This was filtered off and the filtrate tested for vanadium by *P. 58*c*: only 5–10 mgm. V were found.

Separation of Zinc and Vanadium by Hydrogen Sulphide.—H_2S was passed into a solution containing H_3VO_4 and acetic acid: the solution slowly became blue and sulphur separated; the precipitate rapidly became dark-colored, owing to the formation of some V_2S_4.

1 mgm. V as Na_3VO_4 and 50 mgm. Zn as $Zn(NO_3)_2$ were dissolved in

30 ccm., a little acetic acid was added, and an excess of about 3 ccm. NH_4OH (0.90). The clear solution was saturated with H_2S. A heavy precipitate of ZnS separated at once, and the solution slowly became deep red in color, which color was very distinct after filtering. The experiment was repeated with 1 mgm. Zn and 50 mgm. V: a precipitate of ZnS was obtained, which was confirmed by the last paragraph of P. 57.

Action of NH_4OH on Uranium Solutions Containing H_2O_2.—100 mgm. U as $UO_2(NO_3)_2$ were treated by P. 52. The red (peruranate) solution was made acid with HNO_3. Without heating, the acid solution, which contained H_2O_2 (see C. E., P. 52, N. 6), was made alkaline with NH_4OH: a large yellow precipitate of $(NH_4)_2U_2O_7$ separated, but the filtrate was yellow. The filtrate was acidified with HNO_3, boiled for 2 or 3 minutes, and again made alkaline with NH_4OH: a large yellow precipitate separated, which was nearly as large as the first NH_4OH precipitate. The colorless filtrate was again acidified, boiled, and then made alkaline with NH_4OH: no precipitate separated. Therefore uranium, if present, will divide in P. 53.

To a nitric acid solution containing 200 mgm. U as $UO_2(NO_3)_2$ and 40 mgm. V as H_3VO_4 in 40 ccm. were added about 20 ccm. 3% H_2O_2; the mixture was made alkaline with NH_4OH: no precipitate separated, showing that the precipitation of $UO_2NH_4VO_4$ is prevented by the presence of an excess of H_2O_2.

Action of $BaCl_2$ on Uranate Solutions.—100 mgm. U as $UO_2(NO_3)_2$ were treated by P. 52 and 53. The yellow filtrate from the NH_4OH precipitate, which contained about half the uranium, was treated by P. 55: a moderately large precipitate separated. After standing over night the precipitate was filtered off and the filtrate tested for uranium by adding HNO_3, boiling, and adding NH_4OH: a small yellow precipitate separated, which was estimated to contain 2 mgm. U. Therefore barium uranate (or peruranate) may be precipitated nearly completely in P. 55.

Action of $BaCl_2$ on Vanadate Solutions.—100 mgm. V as Na_3VO_4 were treated by P. 52 and 53. See C. E., P. 52, N. 10. The NH_4OH solution, which had a volume of about 40 ccm., was made just acid with acetic acid, and $BaCl_2$ solution was added in the cold as described in P. 55: no precipitate separated from the yellow solution in 5 minutes.—The experiment was repeated with 300 mgm. V: no precipitate appeared when the $BaCl_2$ was first added, but in 10 minutes a large orange precipitate of barium vanadate had separated. This was filtered off and the filtrate allowed to stand over night: a large precipitate formed. The precipitate was collected on a filter and washed with water: much of it dissolved, showing that barium vanadate is fairly soluble in water. A portion of the filtrate which was still slightly yellow was tested for vanadium by *P. 58*e*: much

vanadium was found, showing that the precipitation of barium vanadate takes place slowly, and that large amounts of vanadium remain in the filtrate in the cold.—A solution containing 100 mgm. V as Na_3VO_4 and a little NH_4OH in 40 ccm. was made acid with acetic acid; 10 ccm. 10% $BaCl_2$ solution were added, and the mixture was boiled for a minute or two: a large nearly white precipitate separated, and the solution became perfectly colorless. The precipitate was filtered off and the filtrate tested for vanadium by *P. 58*e*: the filtrate was found to contain not more than a few milligrams of vanadium,' thus showing that a large proportion of the vanadium had been precipitated on boiling.—The last experiment was repeated, except that the acetic acid solution was made alkaline with NH_4OH before boiling: the filtrate was found to be nearly free from vanadium. The last experiment was repeated with a mixture of 100 mgm. V and 10 mgm. Zn as nitrate: only about 3 mgm. Zn were found in the filtrate, showing that a large part of it had been precipitated with the vanadium, probably as zinc vanadate.

Action of NH_4OH on Solutions Containing Zinc, and Vanadium as Vanadate.—500 mgm. Zn as nitrate and 100 mgm. V as Na_3VO_4 were treated by P. 52: only a very small precipitate remained and the solution was colorless. The filtrate was acidified with HNO_3 (1.20), an excess of about 2 ccm. being added; and the solution was made just alkaline with NH_4OH: a large precipitate separated. 4 ccm. NH_4OH (0.96) were added: the precipitate dissolved completely. The NH_4OH solution was neutralized with acetic acid: a large precipitate separated, but it dissolved when a small excess of acetic acid was added. The acetic acid solution was boiled for a minute or two: a large precipitate separated, leaving a clear solution, which, however, still contained considerable zinc and vanadium.

Separation of Zinc and Uranium by NH_4OH.—1 mgm. Zn as $Zn(NO_3)_2$ and 100 mgm. U as $UO_2(NO_3)_2$ were dissolved in 4 ccm. HNO_3 (1.20) and 100 ccm. water; the mixture was made alkaline with NH_4OH and an excess of about 3 ccm. added; the yellow precipitate was filtered off and the solution tested for zinc with H_2S: a small nearly white precipitate separated.—The experiment was repeated with 50 mgm. Zn and 100 mgm. U: the filtrate contained nearly all the zinc. The precipitate was washed, dissolved in HNO_3, diluted to 100 ccm., and treated again with NH_4OH: the filtrate contained only about 2 mgm. Zn. The NH_4OH precipitate was again treated in the same way: the filtrate contained no zinc.

Action of NH_4OH on Solutions Containing Uranium and Chromate.—4 mgm. Cr as K_2CrO_4 and 100 mgm. U as $UO_2(NO_3)_2$ were treated as in the preceding experiment: the filtrate from the NH_4OH precipitate contained nearly all the chromium; the second NH_4OH filtrate was colorless. The experiment was repeated with 50 mgm. Cr and 100 mgm. U: the

filtrate after the second NH_4OH precipitation was nearly colorless, thus showing that little or no chromium was carried down with the uranium.

G. D., § 13: Separation of Titanium and Zirconium by Boiling with Sulphurous Acid.—With regard to the unsatisfactory nature of the process usually employed, see Hillebrand, *Bull. U. S. Geol. Sur.*, No. **176**, 72–73 (1900). A fairly satisfactory quantitative separation of titanium from iron is obtained by boiling a solution (of a volume of about one liter) containing acetic and sulphurous acids. This large volume is impracticable in qualitative analysis, and H. I. Wood and B. E. Schlesinger (*Theses, M. I. T.*, 1901, 1902) devised the following method: "Heat the HCl solution (volume 10–20 ccm.) to boiling, remove the flame, add at once, carefully, NH_4OH until litmus paper is turned distinctly blue; add 30–40 ccm. H_2SO_3 solution and place on the water bath for 15–20 minutes." This method was carefully tested by us. The results were satisfactory with titanium or zirconium alone; and small quantities of these elements were easily detected. But when iron was also present, some of it was carried down. In an experiment with 3 mgm. Fe, 100 mgm. Ti and 100 mgm. Zr as chlorides, no test for iron was obtained in the filtrate, thus showing that this amount of iron had been completely carried down. Also, when 500 mgm. of Fe alone (as $FeCl_3$) were present, some of the $Fe(OH)_3$ precipitated by NH_4OH did not dissolve in the H_2SO_3 solution; and even when ferrous iron was used, some $Fe(OH)_3$ sometimes precipitated during the heating on the water bath. Moreover, the precipitation of titanium and zirconium was usually incomplete when much of these elements was present, especially if the solution was not made distinctly alkaline with NH_4OH. This method is therefore a very unsatisfactory one.

G. D., § 17: Precipitation of Beryllium Phosphate as a Confirmatory Test.—See B. E. Schlesinger, *Thesis, M. I. T.*, 1902; Classen, *Ausgew. Meth. d. Analyt. Chemie*, fifth edition, 1, 715.

1 mgm. Be as $BeCl_2$ was in each of three experiments dissolved in water containing a little HCl; 1 ccm. 10% citric acid and 2 ccm. 10% ammonium phosphate solutions were added, the mixture was made strongly alkaline with ammonia, and it was boiled gently for about 5 minutes in a small flask: a small white crystalline precipitate separated.—The experiment was twice repeated with 2 mgm. Al as $AlCl_3$: no precipitate separated.—The experiment was four times repeated with 0.5 mgm. Be: no precipitate resulted. Therefore this confirmatory test is hardly delicate enough, especially since beryllium has a very low atomic weight.

Test for Zirconium with Turmeric Paper.—The following procedure, recommended by B. E. Schlesinger (*Thesis, M. I. T.*, 1902), was tested: "Dissolve the phosphate precipitate in HF (1 : 5), evaporate to 1 or 2 drops, and dip a piece of turmeric paper into it; heat the paper at 100°

until dry." (Pink color, presence of ZIRCONIUM.) In agreement with the results of Schlesinger, 1 mgm. was found to be the limit of detectability. Even with 2 mgm. the test was not a striking one. Moreover, titanium also caused a pink coloration of the turmeric paper, and the test was more delicate than in the case of zirconium. The blank test with strong HF was not perfectly satisfactory. The results obtained when HCl, instead of HF, was used were practically the same.

P. 51, N. 2: Precipitation of Small Amounts of Various Elements by Ammonia.—0.5 and 1 mgm. of Al, Be, U, and Zr as nitrate, of Fe as $FeSO_4$, of Cr as $Cr_2(SO_4)_3$, of Ti as $TiCl_4$ were dissolved in separate experiments in 4 ccm. HCl (1.12) and 30 ccm. water in small conical flasks; the solutions were neutralized with NH_4OH (0.96) and about 1 ccm. excess added; the mixtures were shaken several times and then allowed to stand a few minutes: in each case the solution was transparent after the NH_4OH was added; but a distinct flocculent precipitate was observed after the shaking and standing. The precipitates were more difficult to see with chromium, aluminum, and uranium than with the other substances, but even in these cases 0.5 mgm. was easily detected.

The experiments with aluminum, uranium, and chromium were repeated in a volume of 100 ccm. containing 4 ccm. HCl (1.12): 1 mgm. Al was near the limit of detectability in a cold solution, but 0.5 mgm. could be easily detected if the solution were heated nearly to boiling and allowed to stand.—With uranium the limit of detectability was 1–2 mgm. in a cold solution, and with chromium it was 2 mgm. in a cold solution; but with 0.5 mgm. Cr the solution became turbid on heating the NH_4OH solution to boiling.

2 mgm. Cr as $KCr(SO_4)_2$ were dissolved in 4 ccm. HCl (1.12) and a little water; the solution was boiled, diluted to 100 ccm., cooled, and made alkaline with NH_4OH (0.96): a very small precipitate was seen after shaking and standing. This was filtered off and the nearly colorless filtrate was heated to boiling: a finely divided, light green precipitate then separated, showing that precipitation of $Cr(OH)_3$ by NH_4OH in the cold is incomplete.

Solubility of Zinc and Nickelous Hydroxides in Solutions Containing NH_4Cl and NH_4OH.—To a number of solutions containing 500 mgm. Zn as $ZnCl_2$ and varying amounts of HCl in 30 ccm. of solution known amounts of NH_4OH (0.96) were gradually added, 1.0 ccm. HCl (1.12) being equivalent to about 1.5 ccm. NH_4OH (0.96). The following table shows the amount of NH_4OH that had to be added (1) before a large precipitate formed, (2) before a distinct odor of NH_4OH persisted after shaking, and (3) before the precipitate dissolved to give a colorless solution:

HCl (1.12) present.	NH_4OH (0.96) required to give a large precipitate.	To give a distinct odor.	To dissolve the precipitate.
2 ccm.	3 ccm.	8 ccm.	11 ccm.
4 ccm.	7 ccm.	11 ccm.	14 ccm.
6 ccm.	11 ccm.	14 ccm.	16 ccm.
8 ccm.	No precipitate.	17 ccm.	. .

The experiment was repeated in a volume of 100 ccm. containing 4 ccm. HCl (1.12): the result was practically the same as in the corresponding experiment with an initial volume of 30 ccm.

The experiments were repeated with 500 mgm. Ni as $NiCl_2$, the initial volume being 30 ccm.: the solution became blue when an excess of NH_4OH was added, but no precipitate separated even when only 2 ccm. HCl were used. In an experiment with no acid, a large green precipitate resulted, which dissolved on adding about 6 ccm. excess NH_4OH after the odor of NH_4OH was persistent.

Precipitation of Cobalt Hydroxide.—The foregoing experiments were repeated with 500 mgm. Co as $CoCl_2$ and 4 ccm. HCl (1.12) in 30 ccm.: when the NH_4OH was added slowly, a moderately large green precipitate was always obtained, which did not dissolve on adding a large excess of NH_4OH; the supernatant solution was reddish brown. The experiments were repeated with 4 and 6 ccm. HCl (1.12), the NH_4OH (3–4 ccm. in excess) being added all at once; no precipitate was obtained, but the solution was red-colored, and darkened on standing, owing to oxidation.—The experiments were repeated in a volume of 100 ccm. containing 4 ccm. HCl (1.12): the results were the same, except that the amount of green precipitate formed was greater than in the smaller volume, and that a larger excess of NH_4OH was necessary, in order to prevent the separation of a precipitate when the excess of NH_4OH was added all at once.

Solubility of Aluminum Hydroxide in Excess of Ammonia.—To a solution containing 10 mgm. Al as nitrate and 4 ccm. HCl (1.12) in 100 ccm. were added in the cold 17 ccm. NH_4OH (0.96); *i. e.*, an excess of about 10 ccm., and the mixture was shaken: the precipitate of $Al(OH)_3$ was filtered off after about 5 minutes, and the filtrate was boiled for several minutes to expel the excess of NH_4OH: a precipitate of $Al(OH)_3$ separated, which was estimated to contain about 3 mgm. Al. The experiment was repeated, except that an excess of only 2 or 3 ccm. NH_4OH (0.96) was used: the filtrate on boiling became turbid, but the amount of aluminum that separated did not exceed 0.5 mgm.

P. 51, N. 3 and 4: Solubility of $Mg(OH)_2$ in NH_4Cl Solutions.—The solubility of $Mg(OH)_2$ in water is about 2×10^{-4} mols per liter. For evidence that the non-precipitation of $Mg(OH)_2$ in moderately dilute solutions containing an ammonium salt depends solely on small OH^- concentration produced by the driving back of the dissociation of NH_4OH, see Lovén, *Z. anorg. Chem.*, **11**, 404 (1896); Treadwell, *Z. anorg. Chem.*, **37**, 326 (1904); Herz and Muhs, *Z. anorg. Chem.*, **38**, 138 (1904).

The following experiments show that enough ammonium salt is produced by the neutralization of the 4 ccm. HCl (1.12) originally present, to prevent the precipitation of $Mg(OH)_2$ even when 500 mgm. Mg are present.—A solution containing 500 mgm. Mg as $MgCl_2$ and 4 ccm. HCl (1.12) in 100 ccm. was neutralized with NH_4OH (0.96) (6 ccm.), and more NH_4OH was added: no precipitate formed when 40 ccm. in all had been added, but the addition of 10 ccm. more gave a precipitate.—The experiment was repeated with an initial volume of 30 ccm. instead of 100 ccm.: 30 ccm. NH_4OH produced no precipitate, even after several minutes, but 40 ccm. did.—The experiment was repeated with 2 ccm. HCl and a volume of 30 ccm.: 15 ccm. NH_4OH (0.96) produced no precipitate, but 20 ccm. did.

Complex Zinc Ammonia Cathion.—$Zn(NH_3)_4^{++}$. See Herz, *Z. anorg. Chem.*, **25**, 225 (1900); Gaus, *Z. anorg. Chem.*, **25**, 236 (1900); Euler, *Ber.*, **63**, 3400 (1903); Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904).

Complex Nickel Ammonia Cathion.—$Ni(NH_3)_4^{++}$. See Dawson and McCrae, *J. Chem. Soc.* **77**, 1239 (1900); Konowaloff, *Chem. Centralblatt*, **1900**, I, 646, and especially Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904).

Behavior of Chromium towards Ammonium Hydroxide.—To a solution containing in 30 ccm. 3–4 ccm. HCl (1.12) and 250 mgm. Cr as $CrCl_3$, freshly prepared by boiling K_2CrO_4 with concentrated HCl, was added NH_4OH (0.96) until after shaking the odor was distinct. The mixture was divided into two parts; one part was filtered at once; to the other part 10 ccm. NH_4OH (0.96) were added, and it was immediately filtered: the former had only a very faint pink color, and on boiling not more than 0.5 mgm. Cr precipitated as $Cr(OH)_3$; the latter was distinctly pink, and on boiling 2–3 mgm. Cr precipitated as $Cr(OH)_3$.—The experiment was repeated, except that an excess of 2 ccm. NH_4OH was added after the odor of NH_4OH was distinct, and that in addition 5 grams solid NH_4Cl were added to one-half of the mixture; both portions were filtered at once: each filtrate was faintly pink; and on boiling that containing no excess of NH_4Cl there resulted a precipitate of $Cr(OH)_3$ estimated to contain 0.5 mgm. Cr; while on boiling the other filtrate no precipitate separated, and the solution remained pink.—The last experiment was repeated, except that the mixtures were allowed to stand 20 hours before filtering: the filtrate containing no excess of NH_4Cl was faintly pink but did not contain

more than 1 mgm. Cr. The second filtrate was highly colored, and on boiling 5 to 10 mgm. Cr precipitated as $Cr(OH)_3$, but the precipitation was not quite complete.—These results show that both NH_4OH and NH_4Cl increase the amount of the pink chromium compound formed, and therefore prove that this compound is a complex ammonia salt and not a chromite. —For the proof that these solutions are unstable, even at room temperatures, see Herz, *Z. anorg. Chem.*, **31**, 357 (1902).

P. 51, N. 6: Precipitation of Phosphates of Calcium, Barium, Magnesium, and Manganese by Ammonium Hydroxide.—To solutions containing 2 mgm. PO_4 as Na_2HPO_4 and 4 ccm. HCl (1.12) in 30 ccm. were added in separate experiments varying amounts of manganese, barium, and magnesium as chloride and of calcium as nitrate. The solutions were then neutralized with NH_4OH (0.96) and about 2 ccm. excess added, making 8 ccm. in all, after which the mixtures were shaken and allowed to stand: 2 and 3 mgm. Mn gave small precipitates after a minute or two, but 1 mgm. gave no precipitate; 10 and 20 mgm. Ca gave large precipitates at once, but 5 mgm. gave no precipitate even in half an hour. 100 mgm. Ba gave a large precipitate at once, and 50 mgm. gave no precipitate in half an hour. 1, 3, and 5 mgm. Mg gave precipitates on shaking.—The experiment was repeated with 10 mgm. PO_4 and varying amounts of barium. 60 mgm. Ba gave a large precipitate at once, but 40 mgm. gave no precipitate, or only a very small one, in half an hour.—The experiment was repeated with 2 mgm. Ca and varying amounts of phosphate: with 30 mgm. PO_4 a precipitate was obtained at once, with 20 mgm. after several minutes, and with 10 mgm. no precipitate appeared in half an hour. On repeating the experiment with 1 mgm. Ca a precipitate was obtained with 30 mgm. PO_4 after a few minutes, but not with 20 mgm.

P. 51, N. 7: Solubility of the Borates of the Alkaline-Earth Elements.—500 mgm. BO_3 as H_3BO_3 and 20 mgm. Ca as chloride were dissolved in 4 ccm. HCl (1.12) and 36 ccm. water, and NH_4OH (0.96) was added until the mixture after shaking just smelled of it: no precipitate separated. The experiment was repeated with 200 mgm. Ba as chloride: no precipitate separated.—The experiment was repeated with 300 mgm. Ba: a small precipitate formed, but it dissolved on adding a little concentrated NH_4Cl solution.—The experiment was repeated with 500 mgm. Mg as chloride: no precipitate resulted.

P. 51, N. 9: Action of Ammonium Hydroxide on Uranyl Solutions.—See Kern, *J. Am. Chem. Soc.*, **23**, 701–705 (1901).

1 and 3 mgm. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 20 ccm. water, and a few drops NH_4OH (0.96) were added: no precipitate separated on standing, nor on boiling. A small quantity of solid $NaNO_3$ was added to the cold solutions: pale yellow precipitates separated at once,

showing that the uranium had been present in the colloidal form.—The experiment with 1 mgm. U was repeated, except that a little NH_4Cl instead of $NaNO_3$ was added: a yellow precipitate separated.

P. 51, N. 9: Uranyl Salts and Diuranates.—See Dittrick, *Z. physik. Chem.*, **29**, 449–490 (1899); Kern, *J. Am. Chem. Soc.*, **23**, 686–726 (1901).

P. 51, N. 10: Completeness of Precipitation of the Sulphides of the Iron Group.—In each of the following experiments the quantity of the element given below was dissolved in 4 ccm. HCl (1.12) and 96 ccm. water; to this solution in the cold were added 9–10 ccm. NH_4OH (0.96), and then $(NH_4)_2S$ solution, drop by drop, until an excess was present. The mixtures were well shaken and then filtered, generally through a double filter. The results were as follows:

With 5 mgm. Mn as $MnCl_2$, a light-colored precipitate formed at once; the filtrate was clear after two filtrations.—With 0.5 mgm. Mn as $MnCl_2$, the result was the same.—With 0.25 mgm. Mn as $MnCl_2$, the solution became turbid in 2 or 3 minutes.—The filtrate in the first two experiments was evaporated almost to dryness; HNO_3 (1.42) was added; the mixture was evaporated to 5 ccm.; $KClO_3$ was added, and the mixture boiled: no precipitate of MnO_2 separated, showing that the precipitation of MnS had been complete.

With 1 mgm. Zn as $Zn(NO_3)_2$, the mixture became turbid at once, and was readily filtered.—With 0.5 mgm. Zn, the result was the same.—The filtrate in the first experiment was evaporated to 5 ccm., made alkaline with NH_4OH, and $(NH_4)_2S$ was added: only an insignificant turbidity appeared, showing that the precipitation of ZnS was practically complete.

With 0.5 mgm. Co as $Co(NO_3)_2$, a black precipitate formed at once, which was readily filtered off.—With 0.1 mgm. Co, the solution became dark-colored at once.

With 0.2 mgm. Fe as $FeSO_4$, the solution became dark-colored at once, and the precipitate was easily filtered off.—With 0.5 mgm. Fe as $FeSO_4$, the result was the same. The filtrate was evaporated to 5 ccm.; NH_4OH and $(NH_4)_2S$ were added: the solution remained colorless.

With 0.3, 0.5, and 1.0 mgm. Tl as Tl_2SO_4, the solutions became dark brown at once and yielded clear filtrates, which when evaporated almost to dryness, and tested for thallium by *P. 65*d*, gave no precipitate of TlI.

With 0.5 and 1.0 mgm. U as $UO_2(NO_3)_2$, distinct flocculent precipitates could be seen after the addition of $(NH_4)_2S$; the filtrates were clear, and the precipitate, when collected on the filter, was yellow in color.—With 0.3 mgm. U as $UO_2(NO_3)_2$, a slight coloration was seen on the filter, but the precipitate could scarcely be seen before filtration.—With 5 mgm. U as $UO_2(NO_3)_2$ the result was the same. The filtrate was evaporated almost to dryness, and was tested for uranium by *P. 58*d* with $K_4Fe(CN)_6$: no

brown coloration was observed.—The last experiment was repeated, except that the filtrate was evaporated to 5 ccm. and NH_4OH and $(NH_4)_2S$ added: no precipitate formed, showing that the precipitation as sulphide in 100 ccm. had been complete.

Nature of the Uranium Precipitate Produced by Ammonium Sulphide.—20 mgm. U as $UO_2(NO_3)_2$ were dissolved in 4 ccm. HCl (1.12) and 96 ccm. water; about 9 ccm. NH_4OH were added and $(NH_4)_2S$, drop by drop, in the cold, until a distinct excess was present: the precipitate was flocculent and had a bright yellow color. After 2 hours it was light brown and in 6 hours dark brown in color.—The experiment was repeated, except that a much larger excess of $(NH_4)_2S$ was added: the precipitate darkened more rapidly. It is evident that $(NH_4)_2U_2O_7$ is first precipitated, contrary to the statements of some text-books, and that the conversion of this substance into UO_2S takes place slowly.

The Existence of Ferric Sulphide (Fe_2S_3).—That Fe_2S_3 is formed when $(NH_4)_2S$ is added to suspension of $Fe(OH)_3$ in dilute NH_4OH has been proved by Stokes (*J. Am. Chem. Soc.*, **29**, 304. 1907). When, however, an acid solution is first saturated with H_2S and then made alkaline with NH_4OH, FeS and not Fe_2S_3 is formed.

P. 51, N. 11: Dark Color of the Sulphide Precipitate as Evidence of Iron, Nickel, or Cobalt.—To solutions containing 500 mgm. Zn as nitrate, 4 ccm. HCl (1.12), and 30 ccm. H_2O, were added in separate experiments 1 and 2 mgm. Ni as nitrate, 1 and 2 mgm. Co as nitrate, 1 mgm. Fe as $FeSO_4$, and 1 mgm. Fe as $FeCl_3$. The mixtures were neutralized with NH_4OH (0.96), and 3 or 4 ccm. excess added, making 10 ccm. in all: a large white precipitate of $Zn(OH)_2$ remained, which was estimated to contain at least 100 mgm. Zn. Colorless $(NH_4)_2S$ was then added as described in P. 51, and the color of the precipitates was compared with that obtained with 500 mgm. pure zinc: the precipitates containing 1 mgm. Fe were nearly black, with a greenish tinge; those containing 2 mgm. Ni and Co were much darker than the pure ZnS; but those with 1 mgm. Ni and Co were only very slightly darker.—The experiments were repeated, except that 4 ccm. more NH_4OH were added in order to dissolve the $Zn(OH)_2$: the results were substantially the same.—A solution containing 500 mgm. Ca and 1 mgm. Ni as nitrates, 1 gram PO_4 as $(NH_4)_2HPO_4$, 4 ccm. HCl (1.12), and 35 ccm. H_2O was made alkaline with NH_4OH (0.96) and 1 ccm. colorless $(NH_4)_2S$ was added: the large white precipitate of phosphate became dark-colored as soon as the sulphide was added.

P. 51, N. 12: Behavior of Nickel towards Ammonium Monosulphide and Polysulphide.—See Lecrenier, *Chem. Ztg.*, **13**, 431, 449 (1889); Anthony and Magri, *Gazz. chim. ital.*, **31**, II, 265 (1901). By boiling the brown solution in the absence of air the last named authors have prepared NiS_4. The

composition of the brown solution is unknown; it may be ammonium sulphonickelate, $(NH_4)_2NiS_{2+x}$, or colloidal nickel persulphide.

That in absence of air nickel is completely precipitated as NiS and the filtrate is colorless, thus proving that the brown solution is due to the presence of polysulphide, has been shown by Lecrenier (*Chem. Ztg.*, **13**, 431, 449. 1889) and Villiers (*Compt. rend.*, **119**, 1263. 1894). The presence of NH_4OH tends to prevent the precipitation of NiS, and it is possible to obtain colorless (or bluish) solutions containing a small excess both of $(NH_4)_2S$ and of nickel.—In the presence of air we have found it almost impossible when working with large amounts of a pure nickel salt to prevent some nickel from passing into the filtrate, giving a brown solution. The amount of nickel in the filtrate increased with the excess of ammonium sulphide used and with the length of exposure to the air.

Some of the brown solutions obtained in these experiments were boiled in small flasks for 3–10 minutes and then filtered: in each case the filtrate was colorless after a single filtration.

Precipitation of Nickel in Ammoniacal Solution by Hydrogen Sulphide.—In several experiments 500 mgm. Ni as $Ni(NO_3)_2$ were dissolved in 30 ccm. water and 4 ccm. HCl (1.12); NH_4OH (0.96) was added until the odor could be detected after shaking and then 3 ccm. more, and H_2S was led into the mixture for 15 minutes: the precipitates were always granular, and the filtrates were clear and colorless; when the precipitates were washed with water containing either H_2S or a very little $(NH_4)_2S$ the wash water was invariably clear.—On repeating these experiments with cold, very dilute solutions of nickel, containing a considerable excess of NH_4OH, dark-colored filtrates containing nickel were obtained; but when the solutions were hot and only a moderate excess of NH_4OH was present, the filtrates were free from nickel.

**P. 51a, N. 1: Test for Vanadate with H_2S in Alkaline Solution.*—To separate solutions containing 3 grams NH_4Cl and 5 ccm. NH_4OH (0.90) in a volume of 110 ccm. were added 0.1, 0.3, and 0.5 mgm. V as vanadate, and the mixtures were saturated with H_2S: in the experiments with 0.3 and 0.5 mgm. V the solutions quickly became dark yellow, then reddish yellow, and finally pink; in that with 0.1 mgm. V the solution finally became faintly pink, but the test was a poor one. Therefore the limit of detectability under these conditions is 0.1 to 0.2 mgm.

The experiment with 0.5 mgm. V was repeated, except that, instead of 5 ccm. NH_4OH (0.90), 1, 2.5, and 10 ccm., respectively, were used: with 1 ccm. and with 2.5 ccm. NH_4OH the pink color was scarcely noticeable; with 10 ccm. a good color was obtained, as with 5 ccm. NH_4OH, but only after passing in H_2S for a longer time. These experiments show that a fairly large *excess of NH_4OH is necessary*.

20 mgm. V as Na_3VO_4 were added to 20 ccm. NH_4OH (0.96) and H_2S was passed in: the color quickly became brown and slowly turned red, becoming after 5 or 6 minutes a deep cherry-red. The solution was divided into two parts. To the first was added an equal volume of water: the red color disappeared in 2 or 3 minutes, but appeared again on resaturating with H_2S. To the second part of the red solution was added an equal volume of NH_4OH (0.96): the color faded slowly (in 4 or 5 minutes), but reappeared on passing in H_2S. These experiments show that the solution must be saturated with H_2S.

1 mgm. V as Na_3VO_4 was dissolved (*a*) in 20 ccm. NH_4OH (0.90), (*b*) in 20 ccm. NH_4OH (0.96), (*c*) in 5 ccm. NH_4OH (0.96) and 15 ccm. water, (*d*) in 2 ccm. NH_4OH (0.96) and 38 ccm. water, (*e*) in 2 ccm. NH_4OH (0.96) and 98 ccm. water. Each solution was saturated with H_2S: a good color was obtained in every case, showing that in the *absence of ammonium salts the test may be obtained at any concentration of NH_4OH.*

A solution containing 1 mgm. V as Na_3VO_4 and 3 ccm. HNO_3 (1.42) in 10 ccm. was neutralized with NH_4OH (0.90), 1 or 2 ccm. in excess being added, and was then saturated with H_2S: a very faint color was obtained.—The experiment was repeated, except that the acid solution was first evaporated to dryness and ignited: a very good test was obtained, showing that the *presence of ammonium salts interferes with the test for vanadium.*

0.5 mgm. V as Na_3VO_4 was added to some HCl (1.20) and the mixture was evaporated twice nearly to dryness to reduce the vanadic acid to hypovanadic acid; 4 ccm. HCl (1.12) were added and 96 ccm. water; the mixture was neutralized with NH_4OH (0.90), an excess of 5 ccm. was added, and H_2S passed in for 10–15 minutes: the solution darkened quickly, became reddish yellow and finally pink; the color was exactly the same as in the experiment described above with 0.5 mgm. V as Na_3VO_4.—The experiment was repeated with 25 mgm. V, which was reduced to hypovanadic acid by long-continued treatment of the hot solution with H_2S: the solution darkened and then became deep red very quickly. The color was the same as in the experiment described above with 50 mgm. V as Na_3VO_4.

1 mgm. V as Na_3VO_4 was dissolved in 18 ccm. water, 2 ccm. 10% NaOH solution were added, and the mixture saturated with H_2S: a deep red color was finally obtained, which was almost the same as that obtained when NH_4OH was used.—The experiment was repeated with 20 ccm. undiluted NaOH solution: the final color was the same, but the solution remained colorless for a long time while the H_2S was being passed through it. Therefore the formation of the red compound does not depend on the presence of NH_4OH or NH_4^+-ion.

**P. 51a, N. 2: Action of Acids on Sulphovanadate.*—0.5 mgm. V as sodium vanadate was dissolved in 100 ccm. water containing about 3 grams NH_4Cl; 5 ccm. NH_4OH (0.90) were added, and the mixture saturated with H_2S; the pink solution was filtered, and then acidified in the cold with acetic acid, stirred, and filtered: a small black precipitate containing sulphur was obtained. This was dissolved by boiling with a little HNO_3 (1.20); the solutions were evaporated to about 2 ccm., and 1–2 ccm. 3% H_2O_2 were added: a faint orange-yellow color resulted, showing the presence of a small amount of vanadium. The experiment was repeated with sodium hypovanadate: the results were the same.

The experiment was repeated with 25 mgm. V: on boiling the filtrate from the precipitate of vanadium sulphide it became blue and sulphur separated. To it 50 mgm. Fe as $FeCl_3$ were added and then an excess of NH_4OH; the mixture was filtered, the filtrate was evaporated to dryness, the residue ignited and dissolved in a very little HNO_3, and a few drops H_2O_2 solution were added: no color appeared, showing that all the vanadium (in excess of 0.1 mgm.) had been carried down with the $Fe(OH)_3$. The sulphide and hydroxide precipitates were dissolved separately in HNO_3, H_2O_2 was added, together with 20–30 ccm. water, and the intensities of the colors compared: it was estimated that about 10 mgm. V were precipitated as sulphide, and the remaining 15 mgm. V with the $Fe(OH)_3$.—The experiment was repeated with 50 mgm. V, a larger amount of $FeCl_3$ being used: the results were similar, thus showing that under these conditions less than half the vanadium is precipitated as sulphide.—In other experiments in which the volume was only 20 to 30 ccm., and the relative proportion of ammonium salt to NH_4OH was smaller, 80–90% of the vanadium was found to be precipitated as sulphide by acetic acid. Even when NaOH was used instead of NH_4OH, the precipitation of vanadium as sulphide was far from complete.

The experiment with 50 mgm. V described in the last paragraph was repeated, except that HCl was used to acidify the cold solution: it was estimated that roughly one-half of the vanadium was precipitated as sulphide and the other half with the $Fe(OH)_3$.—The last experiment was repeated, except that the mixture containing HCl was boiled for about 1 minute: somewhat less than half the vanadium was found in the HCl precipitate.

**P. 51a, N. 3: Complete Precipitation of Vanadium by Ammonium Hydroxide in Presence of Iron.*—See preceding section and C. E., G. D., § 1.

P. 51a, N. 4: Pervanadic Acid.*—See Scheuer, *Z. anorg. Chem.*, **16, 284 (1898); Pissarjewsky, *Z. physik. Chem.*, **43**, 171 and 173 (1903), and **40**, 368 (1902).

Action of H_2O_2 on Vanadic Acid.—In a series of six test tubes, each

of which contained 1 mgm. V as Na_3VO_4, were placed 0, 0.5, 2, 5, 10, and 20 ccm. H_2SO_4 (1.20); each solution was diluted to 20 ccm., and 2 ccm. 3% H_2O_2 added: no change was observed in the tube with no acid; the solution became orange to orange-red in the remaining tubes, and the intensity of the color increased greatly as the concentration of the acid increased.—The experiments were repeated with HNO_3 (1.20): the results were the same.—All the tubes were allowed to stand over night: no changes in the colors were observed.—Ether was added to a number of the solutions and the mixtures shaken: the ether layer remained colorless.

To solutions containing 1 mgm. V as Na_3VO_4 dissolved in 1 ccm. HNO_3 (1.20) were added (*a*) 1 ccm. 3% H_2O_2 and 8 ccm. water, (*b*) 3 ccm. H_2O_2 and 6 ccm. water, and (*c*) 9 ccm. H_2O_2; each solution was diluted to 10 ccm.: the first two solutions were orange-red, but the third solution was practically colorless, thus showing that a large excess of H_2O_2 spoils the test. To the third solution were added 3 ccm. HNO_3 (1.20): the orange-red color reappeared, thus proving again that the test is more easily obtained in the presence of a large excess of acid. To this solution were then added 7 ccm. H_2O_2: the color became much fainter.

The first series of experiments with varying amounts of HNO_3 (1.20) and a total volume of 20 ccm. was repeated, except that 0.1 mgm. V as Na_3VO_4 was used instead of 1 mgm.: all the solutions remained colorless, showing that 0.1 mgm. V cannot be detected in 20 ccm.—This series of experiments was repeated with 0.3 mgm. V: a distinct yellow color could be seen on looking down the tubes in the experiments with 5, 10, and 20 ccm. HNO_3, a slight color with 2 ccm. HNO_3, and none with 0.5 ccm. —This series was repeated with 0.5 mgm. V: with 0.5 ccm. HNO_3 the solution was colorless, with 2 ccm. it was slightly yellow, and in the remaining experiments a slight but distinct orange-yellow color was observed. Therefore the limit of detectability of vanadium with H_2O_2 in HNO_3 solution is about 0.5 mgm. V in 20 ccm., and the solution must contain at least 1 volume HNO_3 (1.20) to 3 volumes of water.

P. 51a, N. 5: Tungstic Acid Dissolves in Acids when Phosphate or Arsenate is Present.*—*Tech. Quart.*, **16, 122 (1903).

Partial Precipitation of Tungsten on Acidifying a Solution of Sulphotungstate.—See *Tech. Quart.*, **17**, 253–255 (1904).

Action of H_2S on Tungstate Dissolved in Excess of NH_4OH.—50 mgm. W as $(NH_4)_2WO_4$ and 3 grams NH_4Cl were dissolved in 100 ccm. water, 5 ccm. NH_4OH (0.90) were added, and the mixture was saturated with H_2S: the solutions remained nearly colorless for over 10 minutes, but finally became slightly yellow, probably owing to the formation of polysulphide.

Action of H_2O_2 on Tungstic and Molybdic Acids.—See *Tech. Quart.*, **17**,

251 (1904).—20 mgm. Mo as $(NH_4)_2MoO_4$ were dissolved in 5 ccm. HNO_3 (1.20), and 2 ccm. H_2O_2 added: a lemon-yellow color resulted. On account of the absence of an orange tint there is no difficulty in distinguishing between this color and that of pervanadic acid.

Action of H_2S on Molybdate Dissolved in Excess of NH_4OH.—A solution containing 6 mgm. Mo as $(NH_4)_2MoO_4$ and 4 ccm. HCl (1.12) in 30 ccm. was treated by P. 51: no precipitate formed with NH_4OH, nor with $(NH_4)_2S$. To the nearly colorless filtrate were added 5 ccm. NH_4OH (0.90), and H_2S was led through the solution in a test tube for 20 minutes. After 3 minutes the solution was dark yellow; after 5 minutes it had a reddish color; after 10 minutes it was brilliant red; and the color did not change in the next 10 minutes. The color was not the same as in the case of vanadium, but might be mistaken for it if a comparative test were not made.—50 mgm. Mo as $(NH_4)_2MoO_4$ and 3 grams NH_4Cl were dissolved in 100 ccm. water, 5 ccm. NH_4OH (0.90) were added, and the solution was saturated with H_2S: the colors obtained were the same as in the preceding experiment. The last experiment was repeated with 1 mgm. Mo: the solution finally became deep orange in color.

Action of Acids on Sulphomolybdate.—50 mgm. Mo as $(NH_4)_2MoO_4$, 3 grams NH_4Cl, and 5 ccm. NH_4OH (0.90) were dissolved in 100 ccm. water, and saturated with H_2S. The red solution was filtered and then made distinctly acid with acetic acid: the color remained nearly the same; on filtering a very small black precipitate was obtained which contained less than 1 mgm. Mo. The solution was allowed to stand for 1 hour: it remained clear. After 3 hours a small precipitate had separated which contained only 2 or 3 mgm. Mo. The mixture was then boiled for 5 minutes and filtered: about two-thirds of the molybdenum precipitated as MoS_3 and the filtrate was still deep orange. The filtrate was evaporated to a small volume and 10 ccm. HCl (1.20) added: a large black precipitate of MoS_3 separated, but the solution was found still to contain 1 or 2 mgm. Mo.

The foregoing experiment was repeated, except that HCl was added to the cold solution: a black precipitate separated at once. The filtrate was evaporated to 30 ccm. and tested for Mo by *P. 43*c*: none was found.—The experiment was repeated, except that the mixture was boiled after adding HCl: the result was the same, not more than a trace of molybdenum being found in the filtrate.

P. 52, N. 3: Formation of Sulphate on Dissolving NiS in Acids.—In two experiments 300 mgm. Ni as freshly precipitated NiS were treated by P. 52; the sulphur was filtered off, and $BaCl_2$ was added to the filtrate: small precipitates of $BaSO_4$ separated, each of which was estimated to contain 5–10 mgm. Ba.—In another series of experiments the NiS was first treated in the cold for several minutes with mixtures of 5 ccm. HNO_3

(1.20) with 20–30 ccm. of water, and the residue was dissolved by evaporating the solution to concentrate the HNO_3, and then adding a few drops HCl (1.20): precipitates of $BaSO_4$ resulted, estimated to contain from 20 to 50 mgm. Ba. In each of these experiments, especially when the precipitate was first treated with HNO_3, considerable sulphur separated and the NiS enclosed in it did not dissolve readily.

P. 52, N. 4: Action of HCl on Titanium and Zirconium Hydroxides.—Acid solutions containing 100 mgm. Ti and 100 mgm. Zr as chlorides in volumes of about 100 ccm. were treated in the cold with NH_4OH; the precipitates were filtered off and treated with 20 ccm. cold HCl (1.12): they dissolved completely in a minute or two.—The experiments were repeated, except that the solutions were heated to boiling, and the NH_4OH was added to the hot solutions: on pouring 20 ccm. HCl (1.12) repeatedly through the filters containing the hydroxide precipitates, almost all of the $TiO(OH)_2$ dissolved, but only a small portion of the $ZrO(OH)_2$ (8–10 mgm. Zr). On pouring a 20 ccm. portion of hot HCl (1.12) repeatedly through the filters, the remainder of the titanium, but only about half the zirconium, dissolved. The remainder of the $ZrO(OH)_2$ was boiled in a casserole with HCl (1.12) for several minutes: it dissolved completely.

P. 52, N. 5: Complete Precipitation of Titanium and Zirconium in the Sodium Peroxide Procedure.—1 mgm. Ti as $TiCl_4$ was treated with NaOH and Na_2O_2 by P. 52, the mixture being boiled for about 4 minutes after the Na_2O_2 was added: a white precipitate separated. The filtrate was made acid with HCl; one-half of it was tested for titanium by adding H_2O_2: no color appeared, showing that the titanium had been completely precipitated. The other half of the filtrate was tested for H_2O_2 by adding excess of $TiCl_4$: no color appeared, showing that the Na_2O_2 had been completely decomposed.—The experiment was repeated with 500 mgm. Ti: the filtrate contained 1 or 2 mgm. Ti. The precipitate was treated with HCl (1.12): nearly all dissolved in the cold and the remainder on warming. The solution was reddish yellow, showing that the precipitate contained some TiO_2.—The HCl solution obtained in the last experiment (containing nearly 500 mgm. Ti) was treated with NaOH and Na_2O_2, by P. 52; the mixture containing Na_2O_2 was boiled for less than 1 minute: the filtrate contained at least 5 mgm. Ti. These experiments show that the amount of titanium that remains in the filtrate may be greatly lessened by long-continued boiling.

1 mgm. Zr as $ZrCl_4$ was treated with NaOH and Na_2O_2 by P. 52: a distinct precipitate separated.—The experiment was repeated with 100 mgm. Zr; the large precipitate was filtered off, and the filtrate was tested for zirconium by acidifying with HNO_3, evaporating almost to dryness, and adding Na_2HPO_4 solution: only a trifling precipitate separated, thus proving that the precipitation of the zirconium had been complete.

P. 52, N. 5: Action of NaOH on Uranyl Salts.—A solution containing 5 mgm. U as UO_2Cl_2 and a little HCl in 15 ccm. was neutralized with 10% NaOH solution, and an excess of 2 or 3 ccm. was added: a small yellowish precipitate separated. This was filtered off and the filtrate was tested for uranium by acidifying and adding NH_4OH: a small precipitate separated, which was estimated to contain 1 or 2 mgm. U.—The experiment was repeated, except that the mixture containing NaOH was boiled for a minute or two: nearly all of the precipitate which had formed in the cold was redissolved. Therefore the uranium is not completely precipitated by a small excess of NaOH.—50 mgm. U as $UO_2(NO_3)_2$ were added to 30 ccm. 10% NaOH solution, and the mixture was heated to boiling, cooled, and poured through a hardened filter; half of the filtrate was tested for uranium as above: only a small precipitate of $(NH_4)_2U_2O_7$ separated, showing that a large proportion of the uranium had been precipitated by the concentrated alkali.

Composition of Sodium Aluminate, Zincate, Beryllate, and Chromite.—For the evidence that sodium aluminate in solution has the formula, $Na^+AlO_2^-$, see Noyes and Whitney (*Z. physik. Chem.*, **15**, 694. 1894), Hantzsch (*Z. anorg. Chem.*, **30**, 296. 1902). Hantzsch has shown by means of conductivity measurements that a solution of the empirical composition Na_2AlO_4 contains mainly NaOH and $NaAlO_2$ and some colloidal $Al(OH)_3$.

Hantzsch (*Z. anorg. Chem.*, **30**, 298, 303. 1902) concluded from conductivity measurements that a $\frac{1}{200}$ molal solution of sodium zincate, even in the presence of a sevenfold excess of NaOH, is almost completely hydrolyzed into NaOH and $Zn(OH)_2$, and that the latter is present as a colloid. Fisher and Herz (*Z. anorg. Chem.*, **31**, 355. 1902) confirmed this by dialysis experiments. Kunchert (*Z. anorg. Chem.*, **41**, 343–348. 1904), working with a larger excess of alkali, and using Bodländer's electromotive force method, proved, however, that the solutions contained chiefly $ZnO_2^=$ and some $HZnO_2^-$.—Förster (*Z. Electrochem.*, **6**, 301. 1899) has prepared solid $NaHZnO_2$.

Hantzsch (*loc. cit.*) concludes that H_2BeO_2 is a very weak acid, weaker than $HAlO_2$, but much stronger than H_2ZnO_2.

From dialysis and conductivity experiments Fisher and Herz (*loc. cit.*) conclude that in alkaline chromite solutions chromium is present almost solely as colloidal $Cr(OH)_3$.

Behavior of Cobalt Hydroxide towards NaOH.—See Donath, *Z. analyt. Chem.*, **40**, 137 (1901).—An acid solution containing 100 mgm. Co as nitrate in 30 ccm. was neutralized with 10% NaOH and an excess of 15 ccm. added; 2 grams Na_2O_2 were added a little at a time to the cold solution, the mixture was boiled for 2 or 3 minutes, cooled, and filtered: the filtrate had a deep blue color. It was acidified, made alkaline with NH_4OH, and H_2S

was passed into it: a precipitate of CoS separated, which was estimated to contain 5–8 mgm. Co.—The experiment was repeated, except that no excess of NaOH was added: the filtrate was colorless and no cobalt was found in it.—This last experiment was repeated, except that 4.5 grams Na_2O_2 were used instead of 2 grams: again the filtrate contained no cobalt. Therefore the blue (soluble) cobalt compound is formed only by the action of concentrated alkali on a *cobaltous* salt; and the cobalt is completely precipitated if it is first oxidized to the cobaltic state by Na_2O_2 in a weakly alkaline solution.

The first experiment with the large excess of NaOH was repeated with 100 mgm. Ni instead of Co: no nickel was found in the filtrate.

P. 52, N. 6: Formation of Peruranates.—See P. Melikow and L. Pissarjewsky, *Z. physik. Chem.*, **28**, 556 (1899).—A large number of salts are known in the solid state; *e.g.*, $UO_4.2Na_2O_2.8H_2O$; $UO_4.2BaO_2.8H_2O$; $UO_4.2CaO_2.10H_2O$, etc. The salts of the alkali elements are soluble in water, the others insoluble. These salts may be regarded as compounds of peruranic anhydride, UO_4, with peroxides of the other elements. They were prepared by the action of H_2O_2 on solutions of uranyl salts in the presence of the hydroxides of the other elements.

An HNO_3 solution containing 100 mgm. U as $UO_2(NO_3)_2$ in 25 ccm. was treated by P. 52: the solution was yellow when acid, and a yellow precipitate separated on adding NaOH; on adding Na_2O_2 (3 grams) and boiling a deep red solution resulted. This solution was acidified with HNO_3: it became yellow. To a portion of it was added a little $TiCl_4$ in HCl solution: an orange-red color resulted, proving the presence of free H_2O_2. Therefore the uranium is oxidized by Na_2O_2 to a soluble "peruranate," which is stable in the strong alkali, but apparently decomposes readily in the acid solution with formation of H_2O_2 and a uranyl salt.—The experiment was repeated, except that only about 0.5 gram Na_2O_2 was added: a yellow uranium precipitate remained, but the solution contained a large proportion of the uranium.

P. 52, N. 7: Complete Decomposition of Na_2O_2 by Boiling.—2 grams Na_2O_2 were added to a neutral solution containing 0.5 gram NaCl in 30 ccm., the mixture was heated to boiling, boiled for 1 minute, cooled, acidified with HNO_3, and tested with $TiCl_4$ solution for H_2O_2; the solution remained colorless.—The experiment was repeated with 100 mgm. Mn as $MnCl_2$, the MnO_2 being filtered off before the filtrate was made acid: it contained no H_2O_2.—The experiment was repeated with 100 mgm. V as Na_3VO_4: the result was the same.—See the preceding paragraph as to the effect of uranium:

Precipitation of Thallium by Sodium Peroxide.—1, 3, and 20 mgm. Tl as $Tl(NO_3)_3$ were treated in separate experiments by P. 52: brown pre-

cipitates separated in each case on adding NaOH, and remained after the treatment with Na_2O_2. The solutions, which were filtered off almost immediately after diluting, were found to contain about 0.5, 1, and 2–3 mgm., respectively.—1 mgm. Tl as Tl_2SO_4 was treated by P. 52: no precipitate separated on adding NaOH; there was a slight coloration on adding Na_2O_2, but no precipitate remained upon boiling; when, however, the solution was set aside to cool, a good precipitate separated in 10 or 15 minutes, and the filtrate was found to contain only 0.2 to 0.4 mgm. Tl.—A mixture containing 1 mgm. Tl as TlCl, 200 mgm. Fe as $FeCl_3$, 200 mgm. Mn as $MnCl_2$, and 200 mgm. Al as $AlCl_3$ was treated by P. 52; the filtrate was evaporated nearly to dryness and tested for thallium by *P. 65*d*: no precipitate of TlI separated.

P. 52, N. 8: Necessity of Adding Na_2CO_3 to Precipitate Barium.—1 and 2 mgm. Ba as $BaCl_2$ were treated by P. 52, the final volume being about 30 ccm.: on boiling, a precipitate which was proved to contain barium appeared in both experiments, but it was very slight in that with 1 mgm. —These experiments were repeated, except that no Na_2CO_3 was added: no precipitates appeared on boiling.

2 mgm. Cr and 100 mgm. Ba as chlorides were treated by P. 52, except that no Na_2CO_3 was added: the filtrate was colorless, and the solution obtained on dissolving the precipitate in HNO_3 was yellow, showing that the chromium had been precipitated as $BaCrO_4$.—The experiment was repeated with 1 mgm. Cr and 100 mgm. Ba, except that Na_2CO_3 was added: the filtrate was yellow, showing that the addition of Na_2CO_3 causes chromium to pass into the filtrate even when a large amount of barium is present.

Solubility of Zinc Carbonate in NaOH.—50 mgm. Zn as nitrate were dissolved in 20 ccm. water and an equivalent amount of Na_2CO_3 added: a white precipitate separated. 5 ccm. 10% more NaOH solution were added: the precipitate dissolved. 5 ccm. more NaOH and 10 ccm. 10% Na_2CO_3 solution were added, and the mixture heated to boiling: no precipitate separated. More Na_2CO_3 was added: a precipitate finally formed.

P. 52, N. 9: Solubility of the Phosphates of Aluminum and Zinc in NaOH.—100 mgm. Zn and 100 mgm. Al as phosphates were dissolved in separate experiments in 25 ccm. water and a very little HNO_3 (1.20); 10% NaOH was added slowly: precipitates separated but dissolved when an excess of about 4 ccm. had been added.

Partial Decomposition of Phosphates on Treating with Sodium Hydroxide.—50 mgm. Mg, 50 mgm. Ca, and 20 mgm. (ferric) Fe, all as freshly precipitated phosphates, were boiled separately with about 30 ccm. 4% NaOH solution for 3 or 4 minutes in covered casseroles; the mixtures were filtered, the precipitates being washed with dilute NaOH. The filtrates were made strongly acid with HNO_3, and the precipitates were dissolved in HNO_3.

Each solution was evaporated to a small volume and treated with several ccm. ammonium molybdate solution. The amount of phosphate in each solution was estimated by the amount of yellow precipitate that had separated out after several hours: in the case of magnesium only a very small proportion of the phosphate remaining in the precipitate; in the case of the iron about one-fifth remained in the precipitate; and in the case of calcium the phosphate was about equally divided between precipitate and filtrate.

Behavior of Calcium Borate and Oxalate towards Sodium Hydroxide.—A mixture containing 100 mgm. Ca as $CaCl_2$ and 80 mgm. BO_2 as H_3BO_3 was treated by P. 52; the precipitate was tested for borate by adding to it in a casserole H_2SO_4 (1.84) and alcohol, igniting the alcohol and stirring vigorously: no green color appeared. The filtrate was acidified with H_2SO_4, evaporated, and tested in the same way: a large amount of borate was found. A trial experiment showed that 5 mgm. BO_2 could easily be detected in this way.

A mixture containing 500 mgm. Fe as $FeCl_3$, 500 mgm. C_2O_4 as oxalic acid, and 100 mgm. Ca as $CaCl_2$ was treated by P. 52; the filtrate was analyzed for oxalate by acidifying, adding NH_4OH and $CaCl_2$: a very large precipitate of calcium oxalate separated.—The experiment was repeated with 300 mgm. Ca and 500 mgm. C_2O_4 (but no iron): the result was the same. The precipitate was tested for oxalate by dissolving it in HCl, and adding NH_4OH: a small precipitate separated, showing that a large proportion of the oxalate had passed into the filtrate.

Decomposition of Oxalic Acid by Acids.—10 and 100 mgm. oxalic acid were treated separately by P. 61, about 1 gram $KClO_3$ being added to the concentrated HNO_3 solution. The solutions were finally evaporated to almost 5 ccm., diluted to 30 ccm., neutralized with NH_4OH, and tested for oxalate by adding 10 ccm. of 10% $Ca(NO_3)_2$ solution: no precipitate separated in either experiment.—The experiment with 10 mgm. oxalic acid was repeated, except that no $KClO_3$ was added to the HNO_3 solution: a precipitate containing about 3 mgm. oxalic acid resulted.—10 mgm. oxalic acid were added to 15 ccm. HCl (1.20), the mixture was evaporated to 2 or 3 ccm., diluted and tested for oxalic acid as above: a precipitate of calcium oxalate separated that was estimated to correspond to 3 or 4 mgm. oxalic acid.—The experiment was repeated with *aqua regia* instead of HCl (1.20): somewhat more oxalic acid was decomposed, but at least 2 mgm. remained.—These experiments prove that the decomposition of oxalic acid is very rapid in a hot mixture of HNO_3 and $HClO_3$, much slower in *aqua regia*, and still slower in HCl (1.20) or HNO_3 (1.42).

P. 52, N. 10: Color of Alkaline Solutions of Sodium Chromate and Peruranate.—1 mgm. Cr as $KCr(SO_4)_2$ was treated by P. 52, the final volume being about 30 ccm.: the yellow color of the solution was easily seen.

1 mgm. U as $UO_2(NO_3)_2$ was treated by P. 52, the final volume being about 15 ccm.; the solution was distinctly yellow.—The experiment was repeated with 5 mgm. U; the solution had a reddish tinge. It was diluted to 30 ccm.: the reddish color changed to yellow.

Color of Vanadium Solutions.—100 mgm. V as Na_3VO_4 were added to a little concentrated HCl, and the mixture was evaporated to a small volume: the solution was at first orange-yellow, but turned greenish blue on evaporation with HCl, showing reduction of the vanadium to the quadrivalent state. Excess of concentrated HNO_3 was added and the mixture again evaporated to a small volume: the solution rapidly became yellow and then deep red, doubtless owing to the formation of vanadic acid. On diluting to about 20 ccm. it became yellow. The solution was neutralized with 10% NaOH solution: a small yellow precipitate separated during the neutralization, but dissolved on the addition of a little more NaOH; the alkaline solution was of a deeper yellow color than the dilute HNO_3 solution. Na_2O_2 was added: no change was observed. The mixture was boiled for 1 minute: the solution became colorless. The solution was cooled and made acid with HNO_3: it became yellow, the color being deepest at the neutral point. To a portion of this acid solution were added 50 mgm. Ti as $TiCl_4$: no change in color was observed, showing that the Na_2O_2 had been completely decomposed and that no pervanadate had remained in the alkaline solution after boiling. Düllberg (*Z. physik. Chem.*, **45**, 172. 1903) considers that the yellow color is due to $HV_4O_{11}^{=}$, an ion of the tetrabasic hexavanadic acid, $H_4V_6O_{17}$ (see C. E., *P. 58*a*, N. 5).

P. 52, N. 11: Division of Zinc in the Sodium Peroxide Treatment.—500 mgm. Fe as $FeSO_4$ and 10 mgm. Zn as $ZnCl_2$ were treated by P. 52, the final volume being about 30 ccm.; the filtrate was tested for zinc by P. 53 and 57: only about 3 mgm. Zn were found, showing that the remainder had been carried down with the $Fe(OH)_3$.—The experiment was repeated with 5 mgm. Zn as $ZnCl_2$: only a trace of zinc was found in the filtrate. —The last experiment (with 5 mgm. Zn) was repeated, except that a large excess of NaOH was added before the Na_2O_2: 1–2 mgm. Zn were found in the filtrate. The precipitate of $Fe(OH)_3$ was analyzed by P. 64, 66, and 67: the remainder of the zinc was found.

500 mgm. Mn as $MnCl_2$ and 10 mgm. Zn as $ZnCl_2$ were treated by P. 52, and the filtrate was tested for zinc by P. 53 and 57; no zinc was found.—The experiment was repeated with 20 mgm. Zn: a very small precipitate of ZnS was obtained in P. 57, which contained less than 0.5 mgm. Zn. On analyzing the precipitate by P. 61, 64, 66, and 67 the zinc was found. Therefore nearly 20 mgm. zinc may be completely carried down when 500 mgm. Mn are present. The experiment was repeated with 10 mgm. Zn, except that the acid solution was poured into a fairly concen-

trated NaOH solution in P. 52: about 0.3 mgm. Zn was found in the filtrate, showing that a little zinc remains in the filtrate in this case.

For the fact that zinc is carried down with nickel and cobalt, see T. A., No. 140–143.

Separation of Vanadium from Manganese.—A mixture containing 250 mgm. Mn as nitrate and 1 mgm. V as Na_3VO_4 was treated by P. 52; the filtrate was tested for vanadium by *P. 58*e*: a very good test was obtained.

P. 53, N. 1: Solubility of Zinc Phosphate, Carbonate, and Oxalate in Ammonium Hydroxide.—100 mgm. Zn as $ZnSO_4$ along with an equivalent amount of sodium phosphate, sodium carbonate, or oxalic acid were dissolved in separate experiments in about 2 ccm. HNO_3 (1.20) and about 30 ccm. cold water. The solutions were neutralized with NH_4OH (0.96) and an excess of about 3 ccm. added: clear solutions were obtained in each case.

P. 54, N. 1–3: Confirmatory Test for Aluminum.—See Knoevenagel, *Praktikum des anorg. Chemikers,* page 160.

0.5 mgm. Al and 0.2 mgm. Co as nitrates were treated by P. 54: the ash retained the form in which the filter paper was rolled and had a brilliant blue color. The experiment was repeated with 0.2 mgm. Al and 0.1 mgm. Co: the residue was distinctly blue. The experiment was repeated with 0.1 mgm. Al and 0.1 mgm. Co: no blue color was apparent.

Effect of Other Elements upon the Confirmatory Test for Aluminum.—0.5 mgm. Al and 0.2 mgm. Co as nitrates were treated by P. 54, except that 1 mgm. Fe as $Fe_2(NO_3)_3$ was also added: the residue was brown. This experiment was repeated with 1 mgm. Al: the residue was partly blue. The experiment was repeated with 2 mgm. Fe and 1 mgm. Al: the blue color could scarcely be distinguished.

The experiment with 0.5 Al was repeated in the presence of 1 mgm. Be as $Be(NO_3)_2$: the residue was blue. The experiment was repeated with 5 mgm. Be: a satisfactory test for aluminum was obtained.—The experiment with 1 mgm. Al was repeated in the presence of 5 mgm. Be and also of 10 mgm. Be as nitrate: a fair test for aluminum was obtained in the presence of 5 mgm. Be, but none with 10 mgm. Be. In the latter case the paper and ash disintegrated.

1 mgm. Al as nitrate was treated by P. 54, in the presence of 1, 2, and 5 mgm. U as $UO_2(NO_3)_2$, respectively: a slight test for aluminum was obtained in the first experiment, a very poor one in the second, and none in the third. The experiment was repeated with 0.5 Al and 1 mgm. U: the test was very poor.

The experiment was repeated with 1 mgm. Al and 5 mgm. V as Na_3VO_4: the residue was distinctly blue.

0.5 mgm. Al as $Al_2(PO_4)_3$ and 0.2 mgm. Co as nitrate were treated by P. 54: the residue was blue.

1 mgm. Al as nitrate was precipitated by adding to it $NaHCO_3$ solution and boiling. The precipitate was filtered off, washed once, and treated by P. 54. The ash fused together into a small mass and no blue color was apparent.—1 mgm. Al and about 5 mgm. Na as nitrates were then treated by P. 54: the result was the same, showing that the failure in the first experiment had been due to the presence of a sodium salt.

50 mgm. SiO_2 as Na_2SiO_3 were dissolved in about 2 ccm. HNO_3 (1.20) and 30 ccm. water, heated to boiling, and made alkaline with NH_4OH: the solution slowly became turbid, and a gelatinous precipitate separated. This was collected on a filter, washed, and a portion of hot HNO_3 (1.20) was poured through the filter two or three times: the silica did not dissolve. The HNO_3 solution was tested for aluminum by P. 54, 0.5 mgm. Co as nitrate being added: the residue was black.—The experiment was repeated, except that 2 mgm. Al as nitrate were also present: a fair test for aluminum was obtained.

P. 56, N. 1: Test for Chromate with Hydrogen Peroxide.—For the constitution and properties of perchromic acid and of other perchromates, see Riesenfeld, *Ber.*, **38**, 1885, 3380, 3578, and 4068 (1905).

In a series of test tubes, each of which contained 0.3 mgm. Cr as K_2CrO_4, were placed 0, 0.5, 2, 5, 10, and 20 ccm. HNO_3 (1.20); each solution was diluted to 20 ccm. 3–5 ccm. ether and 2 ccm. H_2O_2 (3%) were added and the solutions were shaken: in the solution containing no acid and in the solutions containing 5, 10, and 20 ccm. acid, no blue color was obtained; but the remaining two solutions became blue at once, and the blue compound was extracted by the ether on shaking. In the solution containing 2 ccm. HNO_3, the color in the ether layer in contact with the solution disappeared in about half an hour on standing; the color was more brilliant and remained for a longer time in the experiment with 0.5 ccm. HNO_3.—The experiment was repeated with H_2SO_4 (1.20) instead of HNO_3: no color was obtained with no acid or with 10 and 20 ccm. of it; the most brilliant and most permanent color was obtained in the experiment with 0.5 ccm. acid.—The experiment was repeated with 30% acetic acid: in this case the best tests were obtained in the solutions containing 10 and 20 ccm. of acid; with the more delicate solutions only a faint blue color was obtained.

Another series of experiments was performed with solutions that contained 0.3 mgm. Cr as K_2CrO_4, and 2 ccm. HNO_3 (1.20) in about 20 ccm.; 3 ccm. ether and varying amounts of H_2O_2 (3%) were added: with 10 ccm. H_2O_2 no test was obtained, with 5 ccm. a slight one, with 2 ccm. a good test, but with 0.5 ccm. H_2O_2 a much better one.

In all of these experiments in which the blue perchromic acid was formed the blue color disappeared completely in less than 1 hour. In some of them the solution was warmed to 50 or 60°: the blue color disappeared

very rapidly. These experiments prove that perchromic acid is a very unstable substance even in the absence of an excess of H^+ or of H_2O_2, and is still more so at higher temperatures.

Delicacy of the Confirmatory Test for Chromate.—To a solution containing 0.5 ccm. Cr as K_2CrO_4 in 100 ccm. was added a little ammonium acetate solution, 2 ccm. acetic acid, and 1 gram $BaCl_2$: a yellow precipitate separated at once. This was collected on a filter and treated by P. 56: upon the addition of H_2O_2 and ether, a distinct blue color resulted.—The experiment was repeated with 0.2 mgm. Cr: a slight but distinct precipitate and color were obtained.

Reduction of Chromic Acid by Filter Paper.—10 mgm. Cr as K_2CrO_4 were precipitated as lead chromate, and the mixture filtered. The precipitate, with the filter, was placed in a casserole; 10 ccm. water and 5 ccm. HNO_3 (1.20) were added, and the mixture was boiled. The solution turned green in about 1 minute, thus showing that reduction takes place readily.

P. 57, N. 3: Ignition Test for Zinc with Cobalt Nitrate.—0.1, 0.2, and 10 mgm. Zn as $Zn(NO_3)_2$ were treated as described in the second paragraph of P. 57, 0.2 mgm. Co as nitrate being used in each experiment: a distinct green color resulted in the experiment with 0.1 mgm. Zn, a deeper color with 0.2 mgm., and an intense color with 10 mgm.—1 mgm. Zn and 2 mgm. Co as nitrates were treated as described in the last paragraph of P. 57: the residue was green. The residue was then heated strongly: it turned black, showing that when an excess of cobalt is present the test is more delicate if the mixture is not heated strongly.—The experiment was repeated with 2 mgm. Cr and 1 mgm. Zn: a green color resulted, which remained after the residue had been heated strongly.

A solution containing 5 mgm. Zn and 0.5 mgm. Co in HNO_3 was evaporated to dryness in a casserole and the mixture was ignited, first gently and then strongly: the residue was black, owing to the presence of cobalt oxide.—0.3 mgm. Zn and 0.2 mgm. Co as nitrates were treated by the last paragraph of P. 57, except that 5 ccm. of 10% Na_2CO_3 solution were added: only a very faint green color resulted.—The experiment was repeated, except that only 3 drops of Na_2CO_3 solution were added in excess: the green color was mixed with black.—The experiment was repeated, with an excess of 1 ccm. and also with an excess of 0.5 ccm. Na_2CO_3 solution: a distinct green color was obtained.—These experiments show that some Na_2CO_3 must be added, but only a moderate quantity.

A solution containing 0.3 mgm. Zn and 0.2 mgm. Co as chlorides and an excess of HCl was treated by P. 57 (last paragraph), no HNO_3 being added: the residue had no distinct color, showing that HCl cannot be substituted for HNO_3.

**P. 58a, N. 3: Composition of the Zinc and Beryllium Precipitates Pro-*

duced by Sodium Hydrogen Carbonate.—500 mgm. Zn as nitrate were treated by *P. 58*a*, using a total volume of 100 ccm. The precipitate was carefully washed with water and tested for carbonate in the usual way by treating with acid in a flask and passing the gas evolved through $Ba(OH)_2$ solution. A large precipitate of $BaCO_3$ was obtained which corresponded to at least 200–300 mgm. Zn.—The experiment was repeated with 200 mgm. Be: a large amount of carbonate was also found in the beryllium precipitate, the precipitate of $BaCO_3$ being about twice as large as in the experiment with zinc. Parsons states, *J. Am. Chem. Soc.*, **28**, 557 (1906), that the precipitate obtained in a dilute ammonium carbonate solution is a basic carbonate. of beryllium.

Precipitation of Aluminum in Hot Sodium Hydrogen Carbonate Solutions in a Closed Bottle.—Solutions containing 2 mgm. Al as nitrate in 100 ccm. were placed in pressure bottles and 2, 5, and 10 mgm. $NaHCO_3$ added: each of the three solutions quickly became turbid in the cold. The bottles were heated at about 95° in a water bath for half an hour: a flocculent precipitate formed in each case in less than 5 minutes and settled in less than 20 minutes. The bottles were cooled and the precipitates filtered off; the filtrates were evaporated with excess of HNO_3 and tested for aluminum with NH_4OH: little or no precipitate separated, showing that the precipitation of the aluminum had been practically complete in each case.—The experiments were repeated with 1, 1/4, 1/16, and 1/32 grams $NaHCO_3$: the results were the same, except that the precipitation was not complete with 1/32 gram $NaHCO_3$.—The experiment was repeated with 1/64 gram $NaHCO_3$: no precipitate was obtained.—These experiments were repeated, except that the solution was thoroughly saturated with CO_2 gas before adding the $NaHCO_3$: the results were nearly the same.

A solution containing 500 mgm. Al as nitrate in 100 ccm. was placed in a bottle and 4 grams $NaHCO_3$ added: there was a violent evolution of CO_2 gas, a small precipitate formed, and the solution still reacted acid to litmus. 1 gram more $NaHCO_3$ was added: a very large precipitate separated, very little gas came off, and the solution after shaking did not turn blue litmus red. The mixture was heated in the closed bottle at 95° in a water bath for half an hour, cooled, and filtered: the filtrate was found to contain no aluminum. Therefore 500 mgm. Al are completely precipitated when about 5 grams $NaHCO_3$ are added in 100 ccm. of solution.

Precipitation of Zinc Carbonate in Hot Sodium Hydrogen Carbonate Solutions.—Four solutions, each containing 2 mgm. Zn as nitrate, dissolved in 100 ccm. were poured into strong 200 ccm. bottles; to these were added 1, 2, 3, and 5 grams, respectively, of solid $NaHCO_3$; the bottles were corked and shaken until the $NaHCO_3$ dissolved; they were then heated in a water bath at 90–95° for half an hour: all the solutions became slightly turbid

in the cold, and after heating for 5 minutes precipitates could be seen in suspension. After the half-hour's heating the bottles were allowed to cool to about 40°, and the solutions containing 1 and 5 grams $NaHCO_3$ were filtered and tested for zinc by evaporating with HNO_3, adding NH_4OH and acetic acid and passing in H_2S: only a trace of zinc was found in each filtrate, thus showing that the precipitation was practically complete in both 1% and 5% $NaHCO_3$ solutions.—The experiments with 1 and 2 grams $NaHCO_3$ were repeated, except that the solutions were thoroughly saturated with CO_2 gas at room temperature before the $NaHCO_3$ portions were added: the results were the same.

The experiment was repeated with a solution containing 500 mgm. Zn as nitrate in 100 ccm., 2 grams $NaHCO_3$ being added: no precipitate of ZnS separated.—The experiment was repeated with 500 mgm. Zn and 1.5 grams $NaHCO_3$: about 5 mgm. Zn were found in the filtrate, showing that 1.5 grams $NaHCO_3$ is not quite sufficient to precipitate 500 mgm. Zn completely.

Precipitation of Beryllium in Hot Sodium Hydrogen Carbonate Solutions in a Closed Bottle.—A solution containing 1 mgm. Be as nitrate in 100 ccm. was placed in a 200 ccm. bottle; 1 gram $NaHCO_3$ was added, and the mixture was digested in the tightly stoppered bottle at about 95° in a water bath for half an hour: the solution became turbid in less than 5 minutes and a precipitate separated in 10 minutes; on standing in the cold for an hour the precipitate seemed to redissolve to a small extent.—The experiment was repeated with a solution that was saturated with CO_2 gas before the $NaHCO_3$ was added: the result was the same.—These experiments were repeated with 1 mgm. Be and 2 grams $NaHCO_3$: the mixture that had been saturated with CO_2 was distinctly turbid in 15 minutes, while the other was only very slightly turbid after half an hour. The solutions cleared on standing for an hour in the cold.—The last experiments were repeated with 2 mgm. Be and 2 grams $NaHCO_3$: distinct precipitates were obtained corresponding to about 1 mgm. Be, but these redissolved to a considerable extent in the cold.

These experiments were repeated with solutions containing 3–10 grams $NaHCO_3$ in 100 ccm. of solution and varying quantities of beryllium: in the 3% $NaHCO_3$ solution 3 mgm. Be gave no precipitate, but a larger amount did so; in the 5% solution about 15 mgm. Be just remained in solution in 100 ccm.; and in the 10% solution about 75 mgm. Be gave a small precipitate in 50 ccm., while 50 mgm. Be gave only a negligible precipitate.

Solubility of Uranyl Vanadate in Sodium Hydrogen Carbonate Solutions.—Solutions containing 100 mgm. U as $UO_2(NO_3)_2$ and 60 mgm. V as Na_3VO_4 were mixed, a few drops HNO_3 (1.20) were added to dissolve the precipitate, the mixture was diluted to 100 ccm., 2 grams $NaHCO_3$

were added, and the mixture was digested in a closed bottle at 95° for half an hour: no precipitate separated. The mixture was cooled down, 40 mgm. V as Na_3VO_4 were added, making 100 mgm. in all, and the mixture was again heated at 95° for half an hour: no precipitate separated in the hot solution nor in the cold on standing several days.—The experiment was repeated with 100 mgm. U and 100 mgm. V, except that the mixture was first treated with NaOH and Na_2O_2 by P. 52, and that 1.5 grams $NaHCO_3$ were used instead of 2 grams: the result was nearly the same.—100 mgm. U as $UO_2(NO_3)_2$, 100 mgm. V as Na_3VO_4, and 3 grams $NaNO_3$ were treated by *P. 58*a*, 1 gram excess of $NaHCO_3$ being added: a precipitate formed on adding $NaHCO_3$, and a considerable one remained after heating the mixture at 100° in a closed bottle for 30 minutes. The precipitate and filtrate were analyzed for uranium and vanadium by *P. 58*c*–58*e*: the filtrate was found to contain 35–40 mgm. of uranium and all but 10 or 15 mgm. of the vanadium.

The last experiment was repeated, except that the mixture was warmed in a flask at 95° (without allowing it to boil) for 30 minutes: the precipitate that remained was smaller and contained only 10–20 mgm. U and 2–5 mgm. V.—The last experiment was repeated, except that the mixture was boiled for 1 minute in an open flask: the precipitate dissolved completely, and no precipitate formed on cooling, even in 24 hours, showing that uranyl vanadate is more soluble in slightly alkaline carbonate solutions than in those from which the CO_2 is prevented from escaping.

An acid solution containing 50 mgm. V as Na_3VO_4 and 50 mgm. U as $UO_2(NO_3)_2$ was diluted to 100 ccm. and neutralized by adding a little powdered $NaHCO_3$. Then 0.5 gram $NaHCO_3$ was added and the mixture was heated in a pressure bottle at 95° for half an hour: on heating, a large precipitate remained.—To a solution containing 100 mgm. V as Na_3VO_4, 20 mgm. U as $UO_2(NO_3)_2$ and a known excess of HNO_3 (1.20) in 50 ccm. (instead of 100 ccm.) was added just sufficient $NaHCO_3$ to leave 1 gram undecomposed $NaHCO_3$. The mixture was heated in a closed bottle at 95° for half an hour: no precipitate separated. To this solution, after cooling, were added 20 mgm. more U, and the mixture was again heated at 95°: a large precipitate separated in the cold and remained on heating.—The experiment was repeated with 100 mgm. U and 10 mgm. V: no precipitate separated. 10 mgm. more V were added and the heating repeated: a large precipitate separated in the cold and remained on heating.—The last experiment was repeated with 100 mgm. V and 100 mgm. U, and the precipitate and filtrate were analyzed for uranium and vanadium by *P. 58*c*–58*e*: the filtrate was found to contain 20 or 30 mgm. of uranium and all but a few milligrams of the vanadium.

Non-Precipitation of Uranyl Chromate, Phosphate, and Oxalate in the

$NaHCO_3$ Procedure.—To a solution containing 100 mgm. U as $UO_2(NO_3)_2$, 200 mgm. Cr as K_2CrO_4 and a known (small) amount of HNO_3 (1.20) in 100 ccm. was added enough $NaHCO_3$ to leave 1 gram of the undecomposed carbonate; the mixture was heated in a closed bottle at 95° for half an hour: no precipitate separated.—A solution containing 100 mgm. U as $UO_2(NO_3)_2$ and 100 mgm. PO_4 as $NaHPO_4$ was treated by P. 52 and then by *P. 58*a*: no precipitate separated in the $NaHCO_3$ procedure. After cooling, an additional 250 mgm. portion of PO_4 was added and the heating repeated: no precipitate separated.—The experiment was repeated with 100 mgm. V as Na_3VO_4 and 200 mgm. oxalic acid: no precipitate separated.

**P. 58a. N. 4: Precipitation of Aluminum, Zinc, and Beryllium in Hot Sodium Hydrogen Carbonate Solutions in Open Flasks.*—2 mgm. Al as nitrate and 3 grams $NaNO_3$ were dissolved in 100 ccm. water; a little $NaHCO_3$ was added until the mixture after shaking just ceased to react acid to litmus paper; 1 gram more was added; the mixture was heated to about 90° and digested at this temperature in a covered flask on a water bath for half an hour: the precipitate slowly dissolved, except a few small flakes. The mixture was filtered while hot, and the filtrate tested for aluminum by acidifying with acetic acid, adding Na_2HPO_4 and heating to boiling: almost all the aluminum was found in the filtrate.—This experiment was repeated twice with 2 mgm. and with 1 mgm.: the results were the same.—The experiment was repeated twice with 20 mgm. Al: the filtrate contained less than 1 mgm. Al.

The experiments with 2 and 20 mgm. were repeated, except that CO_2 gas was passed through the mixture: the results were nearly the same, except that the filtrate may have contained somewhat more aluminum, showing that there is no advantage in using CO_2 gas.

The experiment with 20 mgm. Al was repeated, except that the mixture was boiled for 1 minute: the filtrate contained 3 or 4 mgm. Al.—The experiment was repeated, except that the mixture was allowed to cool before filtering: the filtrate contained about 1 mgm. Al.—The experiment was repeated with 4 mgm. Al: the precipitate disappeared completely on boiling, but a precipitate separated out on cooling.—The experiment was repeated with 6 mgm. Al: a very small precipitate remained on boiling 1 minute.

1 mgm. Zn as nitrate and 2 grams $NaNO_3$ were dissolved in 100 ccm., 1 gram excess $NaHCO_3$ was added, and the mixture boiled in a flask for 1 minute: the precipitate did not dissolve and was proved to contain zinc by P. 53–57.—The experiment was repeated with 20 mgm. Zn, the filtrate being tested for zinc by acidifying with HNO_3, boiling, adding NH_4OH, and passing in H_2S: no precipitate formed, showing that the zinc was completely precipitated.

10 mgm. Be as chloride and 2 grams $NaNO_3$ were dissolved in 100 ccm.

water, $NaHCO_3$, was added until the mixture after shaking just ceased to react acid to litmus paper; 1 gram more was added; the mixture was boiled for 1 minute, and filtered while hot; the filtrate was acidified with HNO_3, evaporated to about 15 ccm., and tested for beryllium by adding NH_4OH: the filtrate contained only about 0.1 mgm. Be.—The experiment was repeated, except that the mixture was allowed to cool before filtering: the filtrate contained about 0.3 mgm. Be.—The experiment was repeated with 1 mgm. Be: the precipitate remained, on boiling, for 1 minute and did not disappear on standing in the cold for several hours.

These experiments were repeated with solutions containing from 1½ to 5 grams $NaHCO_3$ in 100 ccm. of solution and varying quantities of beryllium: in a 1½% $NaHCO_3$ solution with 1 mgm. Be little or no precipitate remained on boiling 1 minute; in a 2% solution no precipitate remained with 2 mgm. Be, but one remained with 4 mgm.; in a 3% solution 40 mgm. Be dissolved almost completely, but 50 mgm. gave a large precipitate. A comparison of these results with those obtained in a similar series of experiments in closed bottles (C. E., N. 3, above) shows that considerably more beryllium dissolves in concentrated $NaHCO_3$ solutions when the CO_2 is allowed to escape.

**P. 58a, N. 5: Precipitation of Uranium with Aluminum or Beryllium in Hot Dilute Sodium Hydrogen Carbonate Solution.*—See T. A., No. 166–170. In an analysis with 200 mgm. Al and 10 mgm. U, starting at *P. 58*a*, 1 or 2 mgm. U were found in *P. 58*c* and 58*d*.

P. 58a, N. 6: Dissociation Relations of Carbonic Acid.*—See McCoy, *Am. Chem. J.*, **29, 437 (1903).

Dissociation Relations of Chromic Acid.—See Spitalsky, *Z. anorg. Chem.*, **54**, 265 (1907), and Sherrill, *J. Am. Chem. Soc.*, **29**, 1641 (1907). The work of the latter shows that H_2CrO_4 dissociates in steps, first into $HCrO_4^-$ and then into $CrO_4^{=}$, that the $HCrO_4^-$ is a very weak acid, and that the latter even in dilute solution is converted by dehydration in large measure, but by no means wholly, into dichromate-ion ($Cr_2O_7^{=}$).

Condition of Vanadates and Vanadic Acid in Solution.—See Düllberg, *Z. physik. Chem.*, **45**, 129–181 (1903). He considers that in a solution of the composition of Na_3VO_4, which reacts strongly alkaline, the salt is largely hydrolyzed according to the reaction: $2Na_3VO_4 + H_2O = 2NaOH + Na_4V_2O_7$, but his evidence is not convincing.—On adding HCl slowly the results indicate the presence of a tetrabasic acid, $H_4V_6O_{17}$. This is a strong acid, two of the hydrogens splitting off nearly completely in dilute solutions, and the third one to a considerable extent. The yellow color is probably due to the ion $HV_6O_{17}^{=}$. The transition of one form of vanadic acid into another takes place readily, the final equilibrium state being reached fairly quickly. Conductivity and freezing-point determinations make it probable that the formula of sodium metavanadate is $(Na^+)_3V_3O_9^{=}$.

Partial Decomposition of H_2O_2 in the $NaHCO_3$ Treatment.—A mixture containing 100 mgm. U as $UO_2(NO_3)_2$ and 100 mgm. V as Na_3VO_4 was treated by P. 52 and *P. 58*a* and then was acidified with HNO_3: the acid solution before adding the $NaHCO_3$ was red, owing to the presence of pervanadic acid, indicating the presence of much H_2O_2; on neutralizing with $NaHCO_3$ it became yellow; and the final HNO_3 solution was also pale yellow. The solution was tested for H_2O_2 with a titanium solution: a distinct color was obtained. These results show that much but not all of the H_2O_2 had been decomposed.

**P. 58b, N. 2: Detection of Chromic Acid in the Presence of Uranium and Vanadium by H_2O_2.*—A mixture containing 1 mgm. Cr, 100 mgm. U, 100 mgm. Zn and 100 mgm. Al as nitrates, and 100 mgm. V as Na_3VO_4 was treated with NaOH and Na_2O_2 by P. 52: a deep red solution resulted, and there was no residue. The solution was made acid with HNO_3, being cooled carefully during the process. Just enough acid was added to dissolve the precipitate that formed. To about one-fourth of the solution in a test tube was added a little ether and about 1 ccm. H_2O_2: the ether layer became blue. The water layer was red before H_2O_2 was added, showing the presence of pervanadic acid.—The experiment was repeated with 2 mgm. Cr, 100 mgm. U, and 100 mgm. V: the result was the same.—After testing for chromium the remainder of the solution was treated by *P. 58*a*, the solution was cooled, made just acid with HNO_3, and one-tenth of it tested for chromic acid with H_2O_2: a distinct blue color was obtained. The remainder of the solution was made somewhat more strongly acid and evaporated to half its volume; the test for chromic acid was then made with half the solution: no blue color was obtained, showing that the chromic acid had been reduced on boiling.

Action of H_2O_2 on Uranium Salts.—To 10 mgm. U as $UO_2(NO_3)_2$ in 20 ccm. were added 1 ccm. HNO_3 (1.20), 1 ccm. 3% H_2O_2, and a little ether: the yellow color of the solution did not change, and the ether layer remained colorless.

**P. 58b, N. 4: Precipitation of Chromate by Lead Nitrate.*—Several solutions, each containing 0.5 mgm. Cr as K_2CrO_4, 2 grams $NaNO_3$, and 1 gram $NaHCO_3$, in 100 ccm. or 70 ccm. were made distinctly acid with HNO_3, shaken to expel CO_2, and neutralized exactly with NaOH; varying amounts of HNO_3 (1.20) were added, and finally known volumes of a 20% lead nitrate solution. The results are shown in the following table:

Initial volume.	Volume of HNO_3 (1.20).	Volume of lead nitrate solution.	
100 ccm.	1½ ccm.	10 ccm.	Precipitate in 1 or 2 minutes
100 ccm.	2½ ccm.	20 ccm.	Precipitate in 3 or 4 minutes
100 ccm.	5 ccm.	30 ccm.	No precipitate in 30 minutes
70 ccm.	1½ ccm.	10 ccm.	Precipitate in 2 or 3 minutes
70 ccm.	2½ ccm.	10 ccm.	Precipitate very slowly
70 ccm.	2½ ccm.	20 ccm.	Precipitate in 3 to 5 minutes

The last two experiments were repeated with 6 grams $NaNO_3$ (instead of 2 grams): only very small precipitates were obtained in half an hour, even with 20 ccm. $Pb(NO_3)_2$ solution, showing that the presence of much $NaNO_3$ prevents the precipitation of $PbCrO_4$.

Behavior of Vanadate and Uranate towards Lead Nitrate.—Several solutions, each containing 100 mgm. V as Na_3VO_4, 2 grams $NaNO_3$, and 1 gram $NaHCO_3$, in 100 ccm. were acidified with HNO_3, shaken, and then neutralized exactly with NaOH; 1½–3 ccm. of HNO_3 (1.20) and 10–30 ccm. of a 20% lead nitrate solution were added and the mixture allowed to stand 30 minutes: with 3 ccm. HNO_3 there was no precipitate, even with 30 ccm. $Pb(NO_3)_2$; with 1½ and 2 ccm. HNO_3 there was none with 10 ccm. $Pb(NO_3)_2$, but a small one with 20 ccm., which was, however, very slight when 2 ccm. HNO_3 were used. The experiments were repeated with an initial volume of 70 ccm.; the results were nearly the same, except that the precipitates when formed were somewhat larger.

A solution containing 100 mgm. U as $UO_2(NO_3)_2$, 2 grams $NaNO_3$, and 1 gram $NaHCO_3$ in 100 ccm. was neutralized with HNO_3, and an excess of 1 ccm. HNO_3 (1.20) was added; finally, 20 ccm. 20% $Pb(NO_3)_2$ were added: no precipitate separated in several hours.

*Precipitation of Aluminum, Beryllium, and Lead by Sodium Phosphate in *P. 58c.*—0.5, 1, and 2 mgm. Al as nitrate, in solutions containing 2 grams $NaNO_3$, 2 grams NH_4NO_3, 5 ccm. 30% acetic acid, and 2 grams $NaHPO_4.12H_2O$ in a total volume of 100 ccm. were heated to boiling: flocculent white precipitates separated in each case, the results showing that this is a very good method of estimating small amounts of aluminum.

The experiments were repeated with 0.5, 1, and 2 mgm. Be as chloride: flocculent white precipitates resulted, except in the experiment with 0.5 mgm. The filtrate in the experiment with 2 mgm. was estimated to contain about 0.5 mgm. Be.

The experiments were repeated with 1 and 2 mgm. Pb as nitrate: a

distinct precipitate was obtained with 2 mgm., but only a very small one with 1 mgm. Pb.

Oxidation of Hypovanadic Acid by Bromine.—50 mgm. V as Na_3VO_4 and 1 gram Pb as $Pb(NO_3)_2$ were dissolved in 2.5 ccm. HNO_3 (1.20) and 100 ccm. water; the mixture was saturated with H_2S in the cold, filtered, and the filtrate was boiled: the cold solution had a blue color, but on boiling, sulphur separated and the color became deeper. The sulphur was filtered off, bromine water added until the bromine odor was distinct after shaking, and the mixture was boiled: the color was still blue. A small excess of bromine was again added: the solution was still blue.—The experiment was repeated, except that several drops liquid bromine were added and the mixture shaken and allowed to stand 2 or 3 minutes; the bromine was then boiled off: the solution was yellow. The filtrate was treated by *P. 58*c*: no precipitate separated.

Behavior of Vanadyl Salts and Vanadate towards Sodium Phosphate.—50 mgm. V as Na_3VO_4 and 1 gram Pb as $Pb(NO_3)_2$ were dissolved in 2½ ccm. HNO_3 (1.20) and 100 ccm. water; the mixture was saturated with H_2S, filtered, boiled, and filtered again. The blue filtrate was treated by *P. 58*c*, 2 grams $(NH_4)_2SO_4$ and 2 grams Na_2HPO_4 being added: on warming, a large, flocculent, bluish white precipitate separated.—The experiment was repeated, except that the vanadyl salt was first oxidized with liquid bromine, as described in P. 58*b*: no precipitate separated in *P. 58*c*.

P. 58c, N. 1: Precipitation of Uranyl Ammonium Phosphate.*—See Kern, *J. Am. Chem. Soc.*, **23, 705–710 (1901).

Detection of Small Amounts of Uranium.—0.3, 0.5, and 1 mgm. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 100 ccm. water containing 5 ccm. 30% acetic acid and 3 grams $NaNO_2$, and treated by P. 58*c*: white flocculent precipitates separated in each case, but that with the 0.3 mgm. U was very small. The precipitates were filtered off and tested by *P. 58*d*: in the experiment with 0.3 mgm. U the ferrocyanide test failed, but was very satisfactory in the other two cases.—The experiment with 0.3 mgm. U was repeated, except that 0.5, 4, and 6 grams, respectively, $(NH_4)_2SO_4$ (instead of 2 grams) were added: very small precipitates of uranyl ammonium phosphate were obtained in each case, but the ferrocyanide test failed. This shows there is no advantage in adding more than 2 grams $(NH_4)_2SO_4$.—The experiments with 0.5 and 1 mgm. U were repeated, except that no ammonium salt was added: with 1 mgm. the result was satisfactory, but with 0.5 mgm. the ferrocyanide test failed.

The first experiments with 0.3, 0.5, and 1.0 mgm. U were repeated in a volume of 40 ccm., instead of 100 ccm.: a distinct phosphate precipitate resulted in each case, and the ferrocyanide test was satisfactory, even with 0.3 mgm. With 0.2 mgm. a small phosphate precipitate formed, but the

confirmatory test failed.—The experiment was repeated with 1.0 mgm. U, except that 0.3 gram $Na_2HPO_4.12H_2O$ was added, instead of 2 grams: the confirmatory test failed, showing that a large excess of Na_2HPO_4 is necessary.—The experiment with 0.3 mgm. U was repeated, except that 10 ccm. acetic acid were used, instead of 5 ccm.: the confirmatory test failed, showing that a large excess of acetic acid makes the phosphate precipitation less complete.

Separation of Uranium and Vanadium by Phosphate.—100 mgm. U as $UO_2(NO_3)_2$. 50 mgm. V as Na_3VO_4, and 1 gram NH_4NO_3 were dissolved in a few drops HNO_3 and 30 ccm. water. The mixture was neutralized with NH_4OH: a large pale yellow precipitate (of uranyl ammonium vanadate) separated. 10 ccm. 30% acetic acid were added: the precipitate did not dissolve. 5 ccm. 10% ammonium phosphate were added, the mixture was heated to boiling, allowed to stand for 15 minutes, and filtered. The filtrate was tested for vanadium by *P. 58*e*: a large quantity was found. The precipitate was washed with dilute NH_4NO_3 solution, dissolved in dilute hydrochloric acid, and the phosphate precipitation repeated: less than 1 mgm. V was now found in the filtrate. The phosphate precipitate was treated in the same way: less than 0.2 mgm. V was found in it.—The complete experiment was repeated, except that the mixture containing the uranium ammonium vanadate precipitate and the acetic acid was heated to boiling, cooled, and allowed to stand over night before the phosphate was added: the result was the same, showing that the vanadium passes into the filtrate even when it is first precipitated in combination with the uranium.

P. 58c, N. 4: Precipitation of Uranyl Hydrogen Phosphate.*—See Kern, *J. Am. Chem. Soc.*, **23, 705 (1901).

**P. 58d, N. 1: Behavior of Uranyl Salts towards Potassium Ferrocyanide.*—Known amounts of $K_4Fe(CN)_6$ solutions were added to solutions containing 0.5 mgm. U as $UO_2(NO_3)_2$, 1 ccm. HCl (1.12), and 10 ccm. nearly saturated NaCl solution: with 4 ccm. of a 3% ferrocyanide solution a brown color appeared only after 40 minutes; with 10 ccm. a brown precipitate separated in about 10 minutes; while with 10 ccm. of a 10% ferrocyanide solution a precipitate separated in a minute or two; showing that a large excess of $K_4Fe(CN)_6$ is needed to make the test delicate.—The experiment was repeated, except that 0.5 ccm. HCl (1.12) was added instead of 1 ccm., 10 ccm. 3% ferrocyanide solution being used: a brown precipitate separated in a minute or two. This experiment was repeated with 0.1 and 0.05 ccm. HCl (1.12): brown precipitates separated at once. The experiment was repeated without the addition of any acid: no brown color appeared. The experiment was repeated, adding 5 ccm. HCl (1.12): no brown precipitate separated in 1 hour, but the solution became blue and a blue precipitate separated slowly on account of the decomposition of the

ferrocyanide. These experiments show that a little acid must be present, but that much acid makes the test less delicate.

0.1 and 0.2 mgm. U as $UO_2(NO_3)_2$ were treated by *P. 58*d*, a few milligrams PO_4 as Na_2HPO_4 being added: a good test was obtained with 0.2 mgm., but only a very poor one after several minutes with 0.1 mgm., showing that 0.1 mgm. is about the limit of detectability, and that phosphate does not interfere with the detection of 0.2 mgm. U.

The experiment with 0.5 mgm. U and 0.5 ccm. HCl (1.12) was repeated, except that water was added instead of NaCl solution: a dark red color resulted, and no precipitate separated out in 1 hour, showing that NaCl is needed to coagulate the colloid.

Behavior of Vanadyl Salts and Vanadic Acid towards Potassium Ferrocyanide.—5 mgm. V as Na_3VO_4 after evaporation with HCl (whereby it is reduced to vanadyl chloride) were treated by *P. 58*d*: a greenish yellow precipitate separated. The precipitate was filtered off and the filtrate tested for vanadium by *P. 58*e*: only a very faint pink color resulted, showing that the precipitation of the vanadium by the ferrocyanide is nearly complete. The experiment was repeated, except that only 2 drops of HCl were added and the solution was not evaporated: no precipitate separated in half an hour, showing that a small quantity of vanadium in the form of vanadic acid is not precipitated by $K_4Fe(CN)_6$.

**P. 58*e*: Non-interference of Lead with the Vanadium Test.*—A solution containing 2 mgm. Pb as $PbNO_3$ and 0.5 mgm. V as Na_3VO_4 and 2 grams NH_4NO_3 was treated by *P. 58*e*, and the black precipitate of PbS formed was filtered off: on saturating completely with H_2S, the filtrate had the characteristic violet-red color due to vanadium.

P. 58*g*, N. 1: Separation of Aluminum and Beryllium.*—See Havens, *Z. anorg. Chem.*, **16, 15 (1898).

Precipitation of Aluminum as $AlCl_3.6H_2O$.—0.5 mgm. Al as $AlCl_3$ was treated by *P. 58*g*, the total volume of the acid ether mixture being about 15 ccm.: on saturating with HCl gas no precipitate could be seen, but on standing about 15 minutes a distinct crystalline precipitate separated out.

100 and 500 mgm. Al as $AlCl_3$ were treated by *P. 58*g*; the filtrates, which had a total volume of about 70 ccm., were evaporated to about 20 ccm. and made alkaline with NH_4OH: no precipitate separated, but in the second experiment there was a faint turbidity corresponding, perhaps, to 0.1 mgm. Al.

Behavior of Beryllium, Uranium, and Chromium in the Hydrochloric-Acid-Ether Process.—100 mgm. Be as $BeCl_2$ were treated by *P. 58*g*, the final volume being about 30 ccm.: a small precipitate remained. This was filtered off, washed twice, dissolved in a little water, and proved to contain aluminum but no beryllium by boiling in a 10% $NaHCO_3$ solution as described in the second paragraph of *P. 58*h*.

500 mgm. Al and 2 mgm. Be as chlorides were treated by *P. 58*g* in a volume of 60 ccm. and the filtrate was treated by *P. 58*h*: a good test for beryllium was obtained and the amount of beryllium in the filtrate was estimated to be 1 or 2 mgm., showing that very little beryllium was retained by the $AlCl_3.6H_2O$.

100 mgm. U as UO_2Cl_2 were treated by *P. 58*g*, the total volume being 50 ccm.: a clear yellow solution was obtained.

20 mgm. Cr as K_2CrO_4 were boiled with HCl (1.20) to reduce the chromium to the chromic state, and the green solution was treated by *P. 58*g* in a volume of about 30 ccm.: the green color quickly disappeared and a violet precipitate separated. This was filtered off after several hours and the filtrate tested for chromium by evaporating, adding NH_4OH and boiling: a precipitate estimated to contain 5–10 mgm. Cr separated.

P. 58h, N. 1: Separation of Beryllium and Aluminum in Strong Sodium Hydrogen Carbonate Solution.*—See Parsons and Barnes, *J. Am. Chem. Soc.*, **48, 1589 (1906).

200 mgm. Al as nitrate were dissolved in 20 ccm. water and added to a warm solution of 10 grams $NaHCO_3$ in 80 ccm. water; the mixture was heated to boiling in a flask, boiled for 1 minute, and filtered; the filtrate was acidified with HNO_3, evaporated to about 20 ccm., and made alkaline with NH_4OH: no precipitate separated on warming gently, nor on standing.

100 mgm. Al and 1 mgm. Be as nitrates were dissolved in 50 ccm. water and 6 grams $NaHCO_3$ were added; the mixture was heated to boiling, boiled for 1 minute, and filtered while still hot; the filtrate was made acid with HNO_3, evaporated to about 10 ccm., and made alkaline with NH_4OH: a very small precipitate separated, which was estimated to contain 1/20 mgm. Be.—The experiment was repeated with 2 mgm. Be: the result was the same.—The experiment was repeated with 5 mgm. Be: scarcely 1 mgm. Be was found in the filtrate. Therefore small amounts of beryllium cannot be completely separated from 100 mgm. Al by this method.

The precipitate obtained in the first experiment was treated by *P. 58*g* and 58*h*: the beryllium present was estimated to be nearly 1 mgm., showing that this separation with HCl and ether is more satisfactory than that with 10–12% $NaHCO_3$.

Behavior of Iron in Strong Sodium Hydrogen Carbonate Solution and its Precipitation as Sulphide.—2 and 5 mgm. Fe as $FeCl_3$ were treated according to the second paragraph of *P. 58*h*, except that the treatment with H_2S was omitted: small precipitates of $Fe(OH)_3$ were formed in the $NaHCO_3$ solutions, but the precipitation was incomplete, for after acidifying the filtrates and adding NH_4OH, precipitates of $Fe(OH)_3$ were obtained, each

of which was estimated to contain over 1 mgm. Fe.—The experiment with 5 mgm. Fe was repeated, except that 5 ccm. NaOH were added to the $NaHCO_3$ filtrate: no precipitate resulted in the cold, but about 0.5 mgm. Fe as $Fe(OH)_3$ precipitated on boiling. The precipitation was still incomplete, for about 0.5 mgm. Fe was found in the solution on acidifying and adding NH_4OH.

0.5 mgm. Fe as $FeSO_4$ and in a second experiment as $FeCl_3$ were boiled with 30 ccm. 10% $NaHCO_3$ for 1 minute, the mixtures were poured through filters, cooled, and H_2S was passed in for about 3 seconds: the solutions became dark-colored at once. After about 5 minutes the mixtures were filtered: the filtrates were clear, with a faint greenish shade, corresponding to an insignificant quantity of iron; more H_2S caused no further darkening.—The experiment with 0.5 mgm. Fe as $FeCl_3$ was repeated, except that the $NaHCO_3$ solution was not cooled before passing in H_2S: a dark green solution was obtained which ran through the filter, showing that it is better to add the H_2S in the cold. To this solution (which was now cold) was added 2 or 3 mgm. Fe as $FeSO_4$: on filtering after several minutes the filtrate was nearly colorless, and more H_2S gave no precipitate nor color.

**P. 58h, N. 2: Behavior of Uranyl Salts in Strong Sodium Hydrogen Carbonate Solution and on Passing in H_2S.*—50 mgm. U as UO_2Cl_2 (and in another experiment as $UO_2(NO_3)_2$ were dissolved in a little water and added to a solution containing 5 grams $NaHCO_3$, the final volume being 50 ccm.; the mixture was boiled for 5 minutes: no precipitate separated.—The experiment was repeated with 5 mgm. U as UO_2Cl_2 in a volume of 30 ccm., and 10 ccm. 10% NaOH solution were added to the 10% $NaHCO_3$ solution after boiling: no precipitate separated.

To a mixture containing 100 mgm. Al and 20 mgm. U dissolved in 50 ccm. 10% $NaHCO_3$ was added 1 gram NH_4Cl and the mixture was boiled: no precipitate separated.

A mixture containing 100 mgm. Be and 10 mgm. U (but no iron) dissolved in 30 ccm. 10% $NaHCO_3$ solution was saturated completely with H_2S gas: no precipitate separated.

The Separation of Uranium and Beryllium by Potassium Ferrocyanide.—15 and 25 mgm. Be as chlorides in HCl solution were evaporated almost to dryness, 10 ccm. saturated NaCl solution were added, the mixture was cooled, and 5 ccm. 10% $K_4Fe(CN)_6$ solution added: clear solutions resulted which were blue colored, owing to the presence of a small amount of iron in the beryllium; after standing several hours a gelatinous, light-colored precipitate had separated in the experiment with 25 mgm. Be.—The experiment was repeated with mixtures of 1 mgm. U as $UO_2(NO_3)_2$ and with 5, 10, 15, and 20 mgm. Be: a dark red color appeared at once in the

experiments with 5 and 10 mgm. Be, and on standing dark red precipitates settled out. In the experiments with 15 and 20 mgm. the color was somewhat obscured, owing to the presence of the iron.—The experiment with 20 mgm. Be and 1 mgm. U was repeated, except that the iron was first removed from the beryllium solution by P. 52: a good test for uranium was then obtained.

P. 61, N. 1: Solubility of Manganese Peroxide in Nitric Acid in the Presence of Filter Paper.—500 mgm. Mn as $Mn(NO_3)_2$ were treated by P. 52; the $MnO(OH)_2$ precipitate was boiled with 30 ccm. HNO_3 (1.20) in a covered casserole for several minutes: very little of the precipitate dissolved.—The experiment was repeated, except that the filter as well as the precipitate was treated with the nitric acid: on boiling, the filter disintegrated and the precipitate dissolved completely in 10 or 15 minutes.—The last experiment was repeated with HNO_3 (1.42): nearly all of the precipitate dissolved after 5 minutes' boiling, and the remainder on standing over night.—The solution obtained in the last experiment was evaporated to a small volume and diluted to about 15 ccm. The paper was filtered off and the filtrate was treated by P. 61: the manganese was completely precipitated.

P. 61, N. 2: Precipitation of Manganese by Chloric and Nitric Acids.—See Hannay, *J. Chem. Soc.*, **23**, 269 (1878); Ford, *Trans. Am. Inst. Min. Eng.*, 9, 397.

P. 61, N. 3: Separation of Other Elements from Manganese by Chloric and Nitric Acids.—See T. A., Nos. 117, 118.

Iron.—100 mgm. Mn as $MnCl_2$ and 1 mgm. Fe as $FeSO_4$ were treated by P. 52 and P. 61 and the filtrate was tested for iron by P. 64: a good test was obtained.—500 mgm. Mn as $MnCl_2$ and 1 mgm. Fe were treated by P. 52 and then by P. 61; the precipitate and filtrate were tested for iron by evaporating with excess of HCl, diluting, and adding KSCN solution: a distinct test for iron was obtained in the filtrate, but much more iron was found in the precipitate than in the filtrate.

Titanium.—A mixture containing 500 mgm. Mn and 1 mgm. Ti as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH: no precipitate separated, proving that the titanium had been completely carried down with the MnO_2.—This experiment was repeated with 5 and with 50 mgm. Ti: the result was the same in each case.—The experiment was repeated with 50 mgm. Mn and 50 mgm. Ti; the precipitate was analyzed by *P. 62*a* and about half the titanium found in it; the filtrate was evaporated almost to dryness: some of the titanium separated during the evaporation as a white precipitate which did not dissolve readily in HCl, but did in HF.—The experiment was repeated with 50 mgm. Ti in the absence of manganese: no precipitate separated on adding $KClO_4$ nor on evaporating to 5 or 10 ccm.

Zirconium.—A mixture containing 500 mgm. Mn and 2 mgm. Zr as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH: only a very small precipitate separated, showing that most but not quite all of the zirconium had been carried down.—The experiment was repeated with 50 mgm. Zr: the filtrate was found to contain 15 or 20 mgm. Zr. The manganese precipitate was treated by *P. 62*a*: the rest of the zirconium was recovered.

Vanadium.—A mixture containing 250 mgm. Mn as nitrate and 1 mgm. V as Na_3VO_4 was treated by P. 61; the filtrate was treated by *P. 58*c* to test for vanadium: no trace of vanadium was found.—For the fact that vanadium is not carried down by manganese in the Na_2O_2 procedure, see C. E., P. 52, N. 11. The experiment was repeated with 250 mgm. Mn and 10 mgm. V: a mere trace of vanadium was found.—The experiment was repeated with 50 mgm. Mn and 10 mgm. V: not more than 1 or 2 mgm. V was found in the filtrate.—The experiment was repeated with 20 mgm. Mn and 10 mgm. V: the filtrate contained not more than 2 or 3 mgm. V.

Uranium.—A mixture of 250 mgm. Mn as $Mn(NO_3)_2$ and 1 mgm. U as $UO_2(NO_3)_2$ was treated by P. 61; the filtrate was tested for uranium by *P. 58*d*: a good test for uranium was obtained.

Thallium.—15 mgm. Tl as $Tl(OH)_3$ were treated by P. 61: no precipitate separated.—200 mgm. Mn as $MnCl_2$ and 1 mgm. Tl as $TlCl_3$ were treated by this procedure; the filtrate was tested for thallium by the regular procedure: a good test was obtained. The precipitate was dissolved in HCl (1.12) and treated by *P. 65*a* and 65*d*: a very small precipitate of TlI was obtained, which was estimated to contain not more than 0.1 mgm. Tl, showing that thallium is not carried down with the manganese.

Test for Titanium with H_2O_2 in the Presence of Iron, Cobalt, or Nickel.—500 mgm. Fe as $FeCl_3$ were evaporated with a large excess HNO_3 (1.42) to 5 ccm., the dark red solution was diluted to 40 ccm.: it became almost colorless. The solution was divided into two parts, and to one of these 0.5 mgm. Ti as $TiCl_4$ solution was added; to both parts 2 or 3 ccm. H_2O_2 were added: in both a deep yellow color very clearly indicated the presence of titanium.—The experiment was repeated, except that the HNO_3 solution was diluted to about 15 ccm.: the test for titanium was distinct, although the ferric solution was not quite colorless.

500 mgm. Co as $Co(NO_3)_2$ were evaporated with excess HNO_3 (1.42) to 5 ccm.; the red solution was diluted to 15 ccm. and divided into two parts, to one of which 1 mgm. Ti was added; to both about 2 ccm. 3% H_2O_2 were added: the solution containing titanium acquired a distinct yellow tinge.

The experiment was repeated with 500 mgm. Ni as $Ni(NO_3)_2$: the green color of the nickel solution containing titanium changed to olive when the H_2O_2 was added.

P. 62, N. 1: Confirmatory Test for Manganese with Lead Dioxide.—To 1 gram PbO_2 and 10 ccm. HNO_3 (1.20) in a casserole were added in separate experiments 0.5, 0.2, 0.1, and 0.02 mgm. Mn as $MnCl_2$. The mixtures were boiled gently for about 2 minutes in covered casseroles and then poured into test tubes: after the PbO_2 had settled, the color of $KMnO_4$ could be clearly seen, even in the last experiment.—The experiment was repeated without adding $MnCl_2$: a perfectly colorless solution was obtained. —The series of experiments was repeated, except that HNO_3 (1.42) was used: the color of $KMnO_4$ was easily distinguished in each case, but was not so pronounced as with the more dilute acid. Moreover, on standing the pink color faded slowly in the concentrated HNO_3.

To determine whether the test would be satisfactory when the manganese was initially present as MnO_2, 1 mgm. Mn as $MnCl_2$ was treated by P. 61, and the precipitate collected on an asbestos filter; about one-tenth of it (*i. e.*, 0.1 mgm. Mn) was treated by P. 62: the permanganate color was very distinct.

**P. 62a, N. 1: Separation of Titanium and Zirconium from Manganese by Ammonia.*—To a mixture containing 50 mgm. Mn and 50 mgm. Ti as nitrates and 4 ccm. HCl (1.12) in 50 ccm. was added NH_4OH (0.96) very carefully until the mixture was barely alkaline to litmus paper; a white precipitate formed. 2 drops more NH_4OH (0.96) were added and the mixture was heated on a steam bath for 10 minutes: the precipitate remained white. The solution was filtered. The filtrate was tested for titanium by adding more ammonia: no more precipitate separated at once, showing that the precipitation of the titanium was complete. The precipitate was dissolved in hot HCl, the process was repeated, and the filtrate was tested for manganese by adding $(NH_4)_2S$: a precipitate estimated to contain 3 or 4 mgm. Mn separated.—The titanium precipitate was again dissolved and treated in the same way: no manganese was found in the filtrate, showing that the manganese had been completely removed in two separations.—The experiment was repeated, except that the 2 drops of ammonia in excess were not added: only about two-thirds of the titanium precipitated. —The experiment was repeated, except that NH_4OH was added until the odor after shaking was distinct: the NH_4OH precipitate was brown, showing the presence of a large amount of manganese.—The last experiment was repeated, except that 15 grams NH_4Cl were also added: the NH_4OH precipitate was white and contained only about 1 mgm. Mn. These experiments prove that a satisfactory separation is obtained only when the hydroxide-ion concentration is very small.

A solution containing 500 mgm. Mn and 1 mgm. Ti as nitrates and 10 ccm. HCl (1.12) in 60 ccm. was made barely alkaline to litmus paper by means of NH_4OH (0.96); an excess of 2 drops NH_4OH was added

and the mixture was heated for 10 minutes on a steam bath: the precipitate was dark-colored. The precipitate was dissolved in hot HCl and the separation repeated: a small white precipitate resulted, which was practically free from manganese. It was dissolved in HCl, and a little 3% H_2O_2 was added: the solution became deep yellow, showing the presence of titanium.—The experiment was repeated with 500 mgm. Mn and 2 mgm. Zr as nitrates: the results were the same. The final white precipitate was dissolved in hot HCl, the solution was evaporated to a few drops, and a piece of turmeric paper was dipped in it and dried over a small flame: it turned pink, proving the presence of zirconium.

Separation of Zirconium from Manganese by Ammonium Acetate.—A solution of 500 mgm. Mn and 5 mgm. Zr in 10 ccm. HCl (1.12) was just neutralized with NH_4OH; 2 ccm. 30% acetic acid were added, the mixture was diluted to 50 ccm., 6 ccm. 50% ammonium acetate were added, and the mixture was boiled: the precipitate was brown, showing that several milligrams of manganese were present and that the separation was unsatisfactory.

Complete Precipitation of Thallium by Ammonium Hydroxide.—20 mgm. Tl as Tl_2SO_4 were treated with HNO_3 and $HClO_3$ by P. 61, and then with NH_4OH by P. 64: a dark red flocculent precipitate separated. This was filtered off, the filtrate was evaporated nearly to dryness and tested for thallium with KI by *P. 65*d*: no precipitate of TlI separated, showing that thallium had been completely precipitated by the NH_4OH. Since thallous hydroxide is soluble, it follows, also, that thallous compounds are completely oxidized by HNO_3 and $HClO_3$ in P. 61.

P. 64, N. 2: Action of Nitric Acid on Potassium Sulphocyanate.—In each of a number of test tubes 1 ccm. HNO_3 (1.42) was placed; varying amounts of water (from 0 to 15 ccm.), and finally 5 ccm. 10% KSCN solution were added: in each case a red color appeared slowly in the cold, more quickly on warming slightly, and more quickly in the more concentrated HNO_3 solutions.—The red solutions were boiled in casseroles: the color disappeared quickly, and the solutions remained colorless on cooling. More KSCN was added: the color reappeared quickly.—The experiments were repeated with 0.1 mgm. Fe as $FeCl_3$: a red color appeared at once in the cold, but on boiling this color also disappeared in a minute or two. To one of these colorless solutions, after cooling, was added KSCN: the red color appeared at once. To another was added 0.1 mgm. Fe as $FeCl_3$: the solution remained nearly colorless. These experiments show that on boiling with HNO_3 the KSCN is completely decomposed, and therefore that the red color due to nitrous acid cannot be eliminated by boiling.

P. 65, N. 2, 5, and 6: Precipitation of Titanium, Zirconium, and Thallium in the Ammonium Acetate Procedure.—0.5 mgm. Ti as $TiCl_4$ in 100 ccm. was treated by P. 65; a small precipitate separated, which was proved to

contain titanium by *P. 65*b*.—The experiment was repeated with 10 and with 500 mgm. Ti; the filtrates were tested for titanium by evaporating with a little H_2SO_4 to fuming, cooling and adding H_2O_2: no color appeared.

A mixture containing 500 mgm. Fe as $FeCl_3$ and 20 mgm. Zr as $ZrCl_4$ was treated by P. 65: a large amount of zirconium was found in the precipitate, but on adding NH_4OH to the filtrate a white precipitate was obtained, which was estimated to contain 3–5 mgm. Zr.—10 mgm. Zr as nitrate in HNO_3 solution were treated by P. 65, except that no $FeCl_3$ was added: NH_4OH was added only until a very small precipitate of zirconium hydroxide separated, and the solution was still acid when the ammonium acetate was added; the filtrate from the basic acetate precipitate was made alkaline with NH_4OH to test for zirconium: a white precipitate separated, which was estimated to contain 1 or 2 mgm. Zr.—The experiment was repeated with 1 and 2 mgm. Zr, except that NH_4OH was added until the solution was neutral; the filtrate was made acid, evaporated to 20 ccm., and then made alkaline with NH_4OH: no precipitate separated. The last experiment was repeated with 5 mgm. Zr as nitrate and 20 mgm. PO_4 as Na_2HPO_4: no zirconium was found in the filtrate.—For the fact that zirconium is not precipitated in the presence of considerable acetic acid, and that it then prevents the complete precipitation of titanium, see Hillebrand, *Bull. U. S. Geol. Survey*, No. **176**, 72 (1900).

20 mgm. Tl as $TlCl_3$ were treated by P. 65, except that no $FeCl_3$ was added: a brown precipitate separated on boiling and also on adding NH_4OH; the former was two or three times as large as the latter, thus showing that at least 5 mgm. Tl were not precipitated till the NH_4OH was added. The filtrate was evaporated nearly to dryness; H_2SO_4 was added, and the solution when cold was tested for thallium with KI and Na_2SO_3 by *P. 65*d*: a small precipitate of TlI was obtained which was estimated to contain 0.5–1 mgm. Tl.—The experiment was repeated with 1 mgm. Tl: no precipitate resulted on boiling nor on adding NH_4OH. The filtrate was proved to contain the thallium.—The experiment with 1 mgm. Tl was repeated, $FeCl_3$ being added as directed in the procedure: no further precipitate separated on adding NH_4OH to the filtrate. Both precipitate and filtrate were tested for thallium: about half of the thallium was found in the precipitate and the remainder in the filtrate.—The last experiment was repeated with 0.5 mgm. Tl: a small but distinct test was obtained for thallium both in the precipitate containing the iron and in the filtrate.

P. 65a, N. 1 to 3: Extraction of $FeCl_3$ by Ether.*—See Rothe, *Stahl und Eisen*, **12, 1052 (1892), **13**, 333 (1893); Langmuir, *J. Am. Chem. Soc.*, **22**, 102 (1900); Kern, *J. Am. Chem. Soc.*, **23**, 689 (1901).

To determine the best concentration of HCl to use in this extraction, a series of experiments was performed as follows: 500 mgm. Fe as $FeCl_3$

were dissolved in 30 ccm. HCl of known specific gravity, and this solution was treated several times with about 35–40 ccm. ether in a separating funnel as described in the procedure. The amount of $FeCl_3$ extracted in each treatment was estimated by evaporating the ether extract to dryness, adding HCl, and precipitating with NH_4OH. Since the ether used contained no HCl the amount of HCl in the water layer is somewhat decreased in each treatment. The proportion of $FeCl_3$ extracted in each treatment was 4–5% with 8% HCl (sp. gr. 1.04); 95–96% with 18% HCl (sp. gr. 1.09); 99% with 22% HCl (sp. gr. 1.11); and 94% with 25% HCl (sp. gr. 1.125).

With the 22% acid (sp. gr. 1.11) the first extraction took out nearly all the $FeCl_3$ (495 mgm. Fe), the second extraction nearly all of the 5 mgm. Fe remaining, and the third only a fraction of a milligram. A similar result was obtained when 500 mgm. Fe as $FeCl_3$ were precipitated with NH_4OH, the precipitate dried between filter papers, and dissolved in HCl (1.12). This result is in agreement with that of Rothe, who recommends an acid of sp. gr. 1.100 to 1.105; for he shook his ether with HCl of this strength before making the separation.

Molecular Formula of Ferric Chloride in Ether Solution.—See Beckmann, *Z. physik. Chem.*, **46**, 860 (1903).

Extraction of Thallic Chloride by Ether.—15 mgm. Tl as $Tl(OH)_3$ were treated by *P. 65*a*: the solution of $TlCl_3$ in HCl (1.12) had a yellow color, but the water layer was colorless after it was shaken with ether; the ether layer had a yellowish color. The first ether extract contained nearly all the thallium, the second ether extract contained less than 1 mgm., and the water layer after the two extractions was practically free from thallium.

**P. 65a, N. 4: Behavior of Titanium, Zirconium, and Uranium in the Ether Treatment.*—A solution of 50 mgm. Ti as $TiCl_4$ in one experiment, and of 50 mgm. Zr in another, in 30 ccm. HCl (1.11) was shaken with an equal volume of ether; the ether layer was evaporated to dryness in a casserole on a water bath, HCl (1.20) was added and heated, the solution was made alkaline with NH_4OH: no precipitate separated in either case, showing that no titanium or zirconium had dissolved in the ether layer. In the case of titanium the water layer became reddish yellow, owing to the presence of H_2O_2 in the ether, and in the case of zirconium a white precipitate ($ZrCl_4$?) separated in the water layer; but when the ether was expelled by evaporation a clear solution resulted. A white precipitate was also found to result with titanium in an experiment in which 300 mgm. PO_4 were also present.

For proof that uranium is not extracted, see Kern, *J. Am. Chem. Soc.*, **23**, 689 (1901).

**P. 65a, N. 5: Extraction of Iron by Ether in the Presence of Phosphate.*

—500 mgm. Fe as $FeCl_3$ and 300 mgm. PO_4 as ammonium phosphate were dissolved in 30 ccm. HCl (1.09) and treated with ether (35 ccm.) as described in the procedure: about 95% of the iron was extracted in each treatment and the phosphate remained in the water layer.

P. 65b, N. 1: Nature of the Compound of Hydrogen Peroxide with Titanium.*—In regard to the colored solution and the preparation of solid TiO_3, see Schönn, *Z. analyt. Chem.*, **9, 41 (1870); Classen, *Ber.*, **21**, 370 (1888); Levy, *Ann. chim. phys.* (6), **25**, 463 (1892); Melikoff and Pissarjewsky, *Ber.*, **31**, 953 (1898).

Mr. Charles Field, 3d, working in this laboratory, performed the following migration experiment. A colored solution was prepared by rotating for 3 hours pure TiO_3, which had been dried over P_2O_5, with a normal HNO_3 solution which contained 1 mol H_2O_2 per liter. The resulting solution was 0.087 molal with respect to TiO_3. A large U-tube which was partly filled with normal HNO_3 solution was placed in a thermostat at 25°, and the titanium solution was carefully introduced through a tube at the bottom of the U. The surfaces of contact of the two solutions were sharply marked. After a current had passed for 8 hours, one of the surfaces of the red solution had moved 4 ccm. upward toward the cathode and the other boundary had moved away from the anode a nearly equal distance. This proves that the color is due to a cathion containing titanium.

Delicacy of the Hydrogen Peroxide Reaction for Titanium.—0.1 mgm. Ti as chloride was treated by *P. 65*b*: a distinct yellow color appeared on adding the H_2O_2 solution.

P. 65b, N. 2: Precipitation and Separation of Titanium and Zirconium as Phosphate.*—See Hillebrand, *Bull. U. S. Geol. Survey*, No. **176, 75 (1900).

0.5 and 1.0 mgm. Zr and a mixture of 1 mgm. Zr and 100 mgm. Ti as chloride were treated by *P. 65*b*: flocculent precipitates formed in every case within 10 minutes, but were more distinct after half an hour.—100 mgm. Ti alone were treated by *P. 65*b*: no precipitate separated in several hours.

10 mgm. Zr as chloride were treated by *P. 65*b*; the precipitate was filtered off after half an hour and the filtrate made alkaline with NH_4OH: a small precipitate estimated to contain about 0.3 mgm. Zr separated. The result was the same when the filtration was made after 20 hours.—The experiment was repeated, except that only 3 or 4 ccm. phosphate solution were used: the filtrate contained 0.5–1.0 mgm. Zr after half an hour and after 1 hour.—The experiment was repeated, using about 15 ccm. phosphate solution: only 0.1–0.2 mgm. Zr remained in the filtrate after 2 hours.

To a number of solutions, containing 1 mgm. Zr as chloride and varying amounts of H_2SO_4 (1.20) in 15 ccm., were added 5 ccm. 7% $Na_2HPO_4 12H_2O$ solution: with 1 and 2 ccm. of acid the solutions became turbid at

once, and flocculent precipitates settled out within 20 minutes; with 5 ccm. acid the solution remained clear for about 10 minutes, but after 1 hour there was a distinct precipitate; with 10 ccm. acid the solution remained clear for a longer time, and only a minute precipitate separated in 1½ hours.

Precipitation of Titanium with Zirconium Phosphate.—10 mgm. Zr and 10 mgm. Ti as chlorides were treated by *P. 65*b*: the precipitate when collected on a filter was distinctly yellow, and this color remained after washing with water for an hour. About 10 ccm. 15% HF solution were poured through the filter in a celluloid funnel and the solution was treated again by *P. 65*b*: the phosphate precipitate was white, and the titanium in the solution was estimated from the color to be about 1 mgm.—0.1 mgm. Ti and 100 mgm. Zr as chlorides were treated by *P. 65*b*: the solution became distinctly yellow on adding H_2O_2, and the filtrate from the phosphate precipitate was also yellow, showing that titanium is not completely carried down by the zirconium.—(100 mgm. Zr alone gave no color with H_2O_2.)

**P. 65b, N. 3: Precipitation of Thorium as Phosphate.*—2, 5, and 50 mgm. Th as nitrate were treated by *P. 65*b*: white, gelatinous precipitates separated on the addition of Na_2HPO_4, the precipitate being small and forming slowly in the experiment with 2 mgm. Th. In the experiment with 5 mgm. a 10 ccm. portion of HF (1 volume 45% HF to 2 volumes water) was poured several times through the filter; the solution was evaporated with H_2SO_4 to fuming, cooled, diluted, and excess NH_4OH added: no precipitate separated at once and only a very small one on standing an hour.

**P. 65b, N. 4: Behavior of Manganese, Cobalt, Uranyl and Vanadyl Salts in the Tests for Titanium and Zirconium.*—100 mgm. Mn as $MnCl_2$ were treated by *P. 65*b* and 65*c*: with H_2O_2 no color resulted, and no precipitate formed when Na_2HPO_4 was added nor on standing 1 hour. After the addition of just sufficient powdered Na_2SO_3 to reduce the H_2O_2 (determined by testing portions of the solution with Ti solution), no precipitate formed; but when about 1 gram more Na_2SO_3 was added a large precipitate separated.—The experiment was repeated separately with 100 mgm. Co as $CoCl_2$ and with 5 mgm. U as $UO_2(NO_3)_2$: there was no change of color with H_2O_2 and no precipitate with Na_2HPO_4 on adding enough Na_2SO_3 to destroy the H_2O_2. The experiment was repeated with 100 mgm. U as $UO_2(NO_3)_2$: the solution was distinctly yellow before the H_2O_2 was added, and a large white precipitate formed on adding just sufficient Na_2SO_3 to decompose the H_2O_2.

10 and 100 mgm. V as Na_3VO_4 were treated in separate experiments by *P. 65*b* and 65*c*: with the 10 mgm. the color obtained on adding H_2O_2 was similar to that obtained with 3–5 mgm. Ti; with the 100 mgm., however, the color was of a much redder shade than that with titanium; on the

addition of an excess of Na_2SO_3 the color changed at once to blue, showing the presence of a vanadyl salt, and no precipitate had separated in either case after several hours in the cold nor on boiling.

**P. 65c, N. 1: Behavior of Titanium in Acid Solutions towards Sodium Phosphate.*—To a solution containing 0.5 mgm. Ti as chloride and 2 ccm. H_2SO_4 (1.20) in 10 ccm. were added 10 ccm. 7% $Na_2HPO_4.12H_2O$ solution: the solution remained clear for 10 minutes, but had become distinctly turbid in half an hour.—Several solutions containing 10 mgm. Ti as chloride and varying amounts of H_2SO_4 (1.20) were treated in the same way; the flocculent precipitates were filtered off after 10 minutes, and the filtrates were made alkaline with NH_4OH: in the experiment with 2 ccm. acid the filtrate contained 0.5–0.1 mgm. Ti; in that with 3 ccm. acid, 1–3 mgm. Ti; in the experiment with 5 ccm. acid, 3–4 mgm. Ti.

10 mgm. Ti as chloride were treated by *P. 65*b* and 65*c*, and after half an hour the mixture was filtered and the filtrate made alkaline with NH_4OH: a very small precipitate was obtained, containing about 0.5 mgm. Ti.—The experiment was repeated with 0.5 mgm. Ti: the solution became distinctly turbid on decolorizing with H_2SO_3. Half of the turbid solution was heated to boiling: a distinct, flocculent precipitate was obtained. The other half was allowed to stand in the cold for half an hour: the precipitate in this case also became somewhat flocculent.

**P. 65d, N. 1: Test for Thallium with KI.*—0.5, 0.2, and 0.1 mgm. Tl as Tl_2SO_4 were treated by *P. 65*d*, the total volume being about 10 ccm.: a distinct yellow, finely divided precipitate of TlI was obtained in each experiment, even in that with 0.1 mgm. Tl.—For proof that 500 mgm. ferric iron does not interfere with the test, see T. A., Nos. 171–174.

**P. 65d, N. 3: Flame Test for Thallium.*—0.5, 0.2, and 0.1 mgm. Tl were precipitated by *P. 65*d* as TlI. The precipitates were collected on small filters and washed twice with a very little water. The moist filter was removed from the funnel, a looped platinum wire was drawn across its surface to collect a little of the precipitate, and introduced into a colorless gas flame: with 0.5 mgm. Tl the momentary green color was generally seen, but it was sometimes obscured by the yellow flame, due to sodium and to small fibers of paper; with 0.2 and 0.1 mgm. Tl the green color could not be detected with certainty.—The experiments were repeated, except that the TlI precipitates were collected on hardened filters: the green flame was much more brilliant with 0.5 and 0.2 mgm. Tl than in the corresponding experiments with ordinary filter paper; it could, however, scarcely be seen with 0.1 mgm. Tl.

P. 69, N. 1: Potassium Cobaltic Nitrite.—See Fisher, *Pogg. Ann.*, **74**, 115 (1848); Sadtler, *Am. J. Sci.* (2), **49**, 196 (1870); Rosenheim and Koppel, *Z. anorg. Chem.*, **17**. 35 (1898).

P. 69, N. 2: Precipitation of Cobalt with Potassium Nitrite.—0.1 and 0.3 mgm. Co as $CoCl_2$ were treated by P. 69: in each experiment the solution became distinctly turbid within 5 minutes. The experiment was repeated in the absence of cobalt: the solution remained perfectly clear.—For the detection of 0.5 mgm. Co in the presence of 250 mgm. Ni in P. 69, see T. A., No. 127.

500 mgm. Co as nitrate were treated by P. 69; the mixture was shaken well, allowed to stand, and filtered after about half an hour and again allowed to stand: a considerable precipitate again separated.—The experiment was repeated, except that the mixture was heated on a water bath to 50 or 60°, with frequent shaking, for half an hour; it was allowed to cool, and filtered: no precipitate separated in the filtrate, even on standing over night.

Separation of Nickel from Cobalt with Potassium Nitrite.—500 mgm. Co and about 5 mgm. Ni as nitrates were treated by P. 69; after standing 20 hours the mixture was filtered; the filtrate was evaporated almost to dryness with HCl and made alkaline with NaOH: only a very small green precipitate separated, corresponding to not more than 2 mgm. Ni. Half of the cobalt precipitate obtained was treated by P. 70: a very good test for nickel was obtained. The experiment was repeated, except that the mixture was heated on a water bath for half an hour: less nickel was found in the filtrate than in the preceding experiment.

Precipitation of Potassium Nickelous Nitrite.—250 mgm. Ni (previously freed from cobalt by a KNO_2 treatment) was treated by P. 69, except that the volume was cut down to 50 ccm. without, however, altering the total amounts of reagents used: a distinct reddish-colored precipitate separated within 20 minutes, which was proved to contain nickel, but no cobalt, by the borax bead test.—For the action of HNO_2 on nickel salts and the formation of $K_4Ni(NO_2)_6$, see Lang, *J. prakt. Chem.*, **86**, 299 (1862); Hampe, *Lieb. Ann.*, **125**, 346 (1863); and Reichard, *Chem. Ztg.*, **28**, 479, 885, 912 (1904).

P. 70, N. 2: Delicacy of Hypobromite Test for Nickel.—150 mgm. Co free from nickel were treated by P. 70: no precipitate was observed, not even on filtering.—The experiment was repeated, except that 0.15 mgm. Ni as $NiCl_2$ was added: the solution became dark-colored on adding excess NaBrO, but no precipitate collected; it was easily seen, however, on the filter.—0.2 mgm. Ni as $NiCl_2$ was treated by P. 70: a distinct precipitate was obtained on filtering.

Separation of Nickel from Cobalt by Hypobromite.—200 mgm. Co and 0.5 mgm. Ni as chlorides were treated by P. 70: the precipitate was tested for cobalt in the borax bead: no blue color was obtained.

A large number of experiments were performed to determine the proper

conditions for making this separation. In working with cobalt free from nickel it was found that a precipitate of $Co(OH)_3$ always formed when the NaBrO reagent (or bromine water and NaOH) was added very soon after the addition of KCN, and that the necessary interval of time was greatly shortened by increasing the excess of KCN added.

The following experiments show that excess of NaBrO is essential to the precipitation of nickel.—1 mgm. Ni as $Ni(NO_3)_2$ was treated by P. 69; the NaBrO solution was added in small portions, and after the addition of each portion the solution was tested with the starch-KI paper: as long as this paper remained colorless no precipitate of $Ni(OH)_3$ separated; but after the precipitate formed, the paper became blue when dipped into the mixture.—The experiment was repeated with 10 mgm. Ni. As long as the precipitation was incomplete the paper remained colorless, or only a small brown ring was formed on the paper, but after complete precipitation all of the paper immersed in the solution became brown or blue.

P. 70, N. 4: Action of H_2S on Alkaline Tartrate Solutions Containing Nickel or Cobalt.—Villiers, *Compt. rend.*, 119, 1263 (1894); 120, 46 (1895), found that when H_2S was passed into a NaOH solution containing freshly precipitated $Ni(OH)_3$ (but no tartrate) the hydroxide was quickly converted into black nickel sulphide, but that a portion of the nickel passed into solution, giving a deep brown color, proving that the presence of tartrate is not essential for the formation of the brown solution.—0.5 mgm. Ni as nitrate was treated by both parts of P. 70: a deep brown solution was obtained on saturating the alkaline tartrate solution in a test tube with H_2S.—0.1 and 0.2 mgm. Ni as nitrate were dissolved in a little HNO_3 and treated by the second paragraph of P. 70, about 5 ccm. of 10% tartaric acid and 5 ccm. excess of NaOH being added: clear, dark yellow solutions were obtained on saturating with H_2S.—The experiment was repeated with 1 mgm. Ni: on passing in H_2S the solution remained nearly colorless for about 1 minute, but finally a clear, dark brown solution resulted.—The experiment was repeated with 20 mgm. Ni: on saturating with H_2S the liquid in the test tube was opaque and almost black in color. The liquid was filtered: very little precipitate remained on the filter. It was allowed to stand several hours: a black precipitate separated, but the filtrate was still black and opaque.

20 mgm. Co as $CoCl_2$ in a little dilute HNO_3 were treated by the second paragraph of P. 70: a black precipitate separated as soon as the H_2S was led in, and the cobalt was completely precipitated within 1 minute. The mixture was filtered, the filtrate was saturated with H_2S, and the test tube was corked and set aside: the solution remained colorless for several hours. A similar solution was exposed to the action of the air in an open flask: it became dark yellow in about 1 hour, owing to oxidation of the

sulphide and consequent formation of polysulphide.—The experiment was repeated, except that 1 mgm. Ni as $NiNO_3$ was also present; the excess of 10% NaOH was 4 or 5 ccm.; H_2S was led into the solution for about 1 minute and the CoS filtered off: the filtrate was nearly colorless. This was saturated with H_2S: it became brown, the color being such as to indicate that very little of the nickel had been carried down with the cobalt.—This experiment was repeated, except that the H_2S was led through the solution for 5 minutes before the CoS was filtered off: the filtrate was of a lighter brown than before, indicating that over half the nickel had been carried down with the cobalt.—The experiment was repeated, except that the CoS was not filtered off till after 10 minutes: the filtrate was almost colorless and remained so on saturating again with H_2S.—The experiment was repeated, the CoS being filtered off after half an hour: the filtrate was colorless and contained no nickel.—In a similar series of experiments in which a smaller excess of NaOH than 4–5 ccm. was added. The filtrate was light brown after 1 minute, and nearly colorless after 5 minutes, thus showing that there is more danger of losing nickel when the excess of alkali is small; in which case the brown solution is formed more quickly.—This result that NiS is deposited on CoS after the separation of the latter was confirmed by several experiments.

Similar experiments were made with a mixture of 20 mgm. Fe as $FeCl_3$ and 1 mgm. Ni, and with one of 20 mgm. Mn and 1 mgm. Ni: good tests for nickel were obtained in both cases.

PROCEEDINGS OF THE SOCIETY OF ARTS

FORTY-SIXTH YEAR, 1907-1908

BOSTON, October 25, 1907.

THE 639th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, October 25, at eight o'clock, about thirty-five persons being present. Colonel Edmund H. Hewins, chairman of the Executive Committee, presided.

The chairman introduced Mr. F. A. Beebee, with the Griffin Wheel Company, of Chicago, who spoke on the manufacture of "Chilled Car Wheels." The lecture was illustrated with a number of lantern slides and gave an interesting *résumé* of car wheel manufacture from the earliest days. The thanks of the Society were tendered the speaker by the chairman, and the meeting adjourned at 9.30 o'clock.

BOSTON, November 14, 1907.

The 640th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Friday evening, November 14, at eight o'clock, one hundred and ten persons being present. Professor T. A. Jaggar, Jr., presided. The name of John Reed was presented for membership, to be voted on at the next meeting.

The chairman introduced Professor Douglas W. Johnson, of Harvard University, who spoke on the "Physical History of the Grand Cañon District." Professor Johnson had spent some time in the field, studying the physical history of this great district, and clearly illustrated its peculiar features both by diagrams on the blackboard and by numerous lantern slides. The speaker gave a most interesting talk, which was fully appreciated by all. The meeting adjourned at 9.30 o'clock.

BOSTON, December 5, 1907.

The 641st regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, December 5, at eight o'clock, about thirty persons being present. Professor C. H. Peabody presided. Mr. Reed was elected a member of the Society.

The chairman introduced Mr. Norman H. Cheney, Chief Engineer of the Merchants' Cold Storage and Freezing Company, of Providence, Rhode Island, who gave a most interesting talk on the manufacture of ice and refrigeration. The address was illustrated with numerous lantern slides The meeting adjourned at 9.30 o'clock.

BOSTON, December 19, 1907.

The 642d regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, December 19, at eight o'clock, about one hundred and thirty persons being present. Dr. C. J. H. Woodbury presided.

The following resolutions were read by the Secretary, on behalf of the Executive Committee, and referred to the Society for action.

RESOLUTIONS IN REGARD TO THE WHITE MOUNTAIN AND APPALACHIAN FOREST RESERVES

Whereas, There have been introduced, or are about to be introduced, in the Congress of the United States a bill or bills providing for the setting apart as Forest Reserves of certain areas in the White Mountains and the Southern Appalachians, and

Whereas, It is the duty of all friends of the proposed legislation to uphold the hands of their representatives in Congress by showing their interest in, and desire for, such legislation, therefore be it

Resolved, That the SOCIETY OF ARTS, at this meeting held in Boston, Massachusetts, December 19, 1907, thoroughly approves and endorses the proposal to set apart such Forest Reserves, and urges the Senators and Representatives from the Commonwealth of Massachusetts in the Sixtieth Congress assembled to give their earnest support and effective aid to the framing of such legislation as they may deem wise for this end.

Resolved, That the SOCIETY OF ARTS approves of this legislation for the following reasons:

1. The presence of forests upon mountain areas is essential to the equable flow of streams arising from them. When forests have been

removed, the soil, no longer protected by the foliage and roots of the trees, is washed from the rocks, which, becoming bare, shed water like the roof of a house; and the streams lose their constant flow, becoming alternately raging torrents and dry water courses.

The forested areas which it is proposed to set apart as Forest Reserves include the head waters of many streams which are of the greatest importance to the life of the people, not only of the regions through which they flow, but of the whole United States. They are of importance to the cities situated in the valleys below as sources of water supply. They are of importance to the manufacturing interests because of the water power which they furnish, and which is just beginning to be developed — a source of power which will be of greater importance to the country as a whole, with the disappearance of our coal supply and with the perfection of the art of transmitting power by electricity.

2. The extensive forests covering the eastern area of the United States have formed one of the most important portions of the national wealth. This has been largely depleted by extravagant wastefulness, and heretofore no national action has been taken to preserve to the people of the United States any part of this wealth east of the Mississippi River. It is, therefore, desirable that these portions should be set apart without delay, that they may be preserved to the use of the people of the whole of the United States.

3. While there are extensive Forest Reserves already set apart in the Western states, the lack of such Reserves in the originally much larger forested area of the East has left the Forest Service without adequate area where experimental forestry may be conducted under the different conditions to be found in this part of the country.

It is, therefore, desirable that such Reserves should be made where it may be determined what are the best methods of planting and harvesting the forest crop, and where operations may be carried on which will not only be a source of revenue to the government, but which will be object lessons to the land owners of the adjoining states.

4. Recreation in the open air and in contact with nature in its most pleasing aspects is essential to the mental, moral, and physical health of men and women of all ages, and especially to the youth. The proposed Forest Reserves would supply an enduring opportunity for such recreation, and would, therefore, be an important factor in the preservation of the national health.

Resolved, That the Secretary of the Society be requested to transmit a copy of these resolutions to the President of the Senate and the Speaker of the House of Representatives, and to each of the Senators and Representatives representing Massachusetts in the present Congress.

It was voted that the consideration of these resolutions be reserved until after the address.

The chairman then introduced Mr. Philip W. Ayers, State Forester of New Hampshire, who gave a most interesting and instructive address on the general features of forestry, particularly in regard to the need of government protection for the forest supply of the country. He brought out very clearly the relation of the present high prices of lumber to the waning timber supply, and clearly showed the need of a careful husbanding of our present supply if we would prevent exorbitant lumber prices in a few years to come. The address was illustrated with numerous lantern slides.

After the address it was moved and seconded that the Society adopt the resolutions read previously in regard to the White Mountain and Appalachian Forest Reserves, and that a copy of these be sent to each Senator and Representative in Congress from New England. This motion was unanimously carried. The meeting adjourned at 9.50 o'clock.

BOSTON, January 9, 1908.

The 643d regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, January 9, at eight o'clock, about one hundred and twenty persons being present. Dr. William H. Walker presided.

The chairman introduced Mr. Rufus F. Herrick, who discussed in a most interesting manner "Denatured Alcohol,"[1] with special reference to its application in the arts. The lecture was illustrated by a number of lantern slides, showing various forms of distilling apparatus used in the manufacture of the alcohol, and the speaker showed various forms of alcohol lamps, stoves, etc., and specimens of various forms of manufactured articles in the production of which alcohol was an essential feature. He gave some interesting figures, illustrating the cost of alcohol from various sources and the effect of different denaturizing formulæ in special lines of work.

After extending the thanks of the Society to the speaker, the meeting adjourned at 9.30 o'clock.

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[1] Printed in full above, pp. 4–11.

PUBLICATIONS[1]

Chemistry and Chemical Engineering

Gilbert N. Lewis.—The Specific Heat of Solids at Constant Volume, and the Law of Dulong and Petit. *Journal American Chemical Society,* Vol. XXIX, p. 1165. *Zeitschrift für anorganische Chemie,* Vol. LV, p. 200.

Gilbert N. Lewis.—Outlines of a New System of Thermodynamic Chemistry. *Proceedings American Academy,* Vol. XLIII, p. 259. *Zeitschrift physikalische Chemie,* Vol. LXI, p. 129.

W. H. Walker.—The Chemistry of Cellulose. *Journal Franklin Institute,* Vol. CLXIV, pp. 131–140. August, 1907.

Under the generic name "cellulose" is included the organic material which forms the skeleton or framework of all vegetable structure from the microscopic unicellular bacterium to the giant conifers of Yosemite. While answering to the same empyrical formula, $C_6H_{10}O_5$, cellulose from different plants presents, however, widely different forms, with an accompanying variation in their chemical properties.

This paper is more particularly concerned with the various forms of cellulose as affected by the chemical reactions of hydrolysis and esterification. The work of previous investigators is discussed, and methods for preparing certain new forms of hydrocellulose are described. The acetic esters as prepared from hydrocellulose, $(C_6H_{10}O_5)_6H_2O$, have properties not possessed by other derivatives of cellulose, which make these compounds of considerable value along a number of technical lines.

Among the more important applications for these cellulose acetates may be mentioned the insulation of very fine wire for electrical purposes, the manufacture of non-inflammable biograph negatives or films, and the preparation of artificial silk.

William H. Walker.—The Annealing of Sterling Silver. *Journal of American Chemical Society,* Vol. XXIX, pp. 1198–1203. August, 1907.

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[1] In order that the extent of productive work carried on at the Institute may be better known, it is designed to publish quarterly a list of the publications of officers of the Institute, together with abstracts when possible. In this list the publications are arranged alphabetically by departments and then alphabetically by authors.

The asterisk after the title indicates that a copy of the publication has been placed in the library of the Institute.

of construction of several makes of lamps; photometric units and descriptions of several forms of photometers. Chapter XVII describes various forms of switches and circuit breakers. Chapter XVIII deals with conductors and insulators. H. G. C.

Electro-Analysis[1]

This edition of this well-known and valuable treatise on electro-analysis differs from previous editions principally in the addition of chapters on the rapid precipitation and separation of metals, the use of the mercury cathode, and in the recent methods worked out by the author and his students for the rapid analysis of the anions. All of the good features of the old editions have been retained and the most recent additions to the science have been included. The introduction of the rotating electrode has modified electro-analysis very considerably, results being obtained now in an hour or less when formerly twenty to twenty-four hours were required. The latest devices for rotating the electrodes and the application of this process to analyses of various kinds are fully discussed. The magnetic rotation of the electrolyte has also been studied, and the apparatus necessary for carrying out this operation is described.

The most novel portion of the book is the description of methods for the rapid analysis of salts for the anions.

The chlorides, bromides, iodides, and, in fact, all salts forming insoluble silver salts may be electrolyzed and the anion deposited on a silver electrode in the form of the silver salt. In the same operation the base may be deposited in a mercury cathode and subsequently determined after reversal of the current by means of a standard acid.

The book has been brought completely up to date and is presented in a new and attractive binding. It is sincerely hoped that the author will in future editions give detailed directions for the complete and rapid analysis of commercial products, such as the brasses, bronzes, and various other alloys. Henry Fay.

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[1] Electro-Analysis. By Edgar F. Smith. Philadelphia: Blakiston, 1907. Edition 4. vi + 336 pp.

PUBLICATIONS[1]

CHEMISTRY AND CHEMICAL ENGINEERING

Gilbert N. Lewis.—The Specific Heat of Solids at Constant Volume, and the Law of Dulong and Petit. *Journal American Chemical Society*, Vol. XXIX, p. 1165. *Zeitschrift für anorganische Chemie*, Vol. LV, p. 200.

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This paper is more particularly concerned with the various forms of cellulose as affected by the chemical reactions of hydrolysis and esterification. The work of previous investigators is discussed, and methods for preparing certain new forms of hydrocellulose are described. The acetic esters as prepared from hydrocellulose, $(C_6H_{10}O_5)_4H_2O$, have properties not possessed by other derivatives of cellulose which make these compounds of considerable value along a number of technical lines.

Among the more important applications for these cellulose acetates is mentioned the insulation of very fine wire for electrical purposes, the preparation of non-inflammable biograph negatives or films, and the production of artificial silk.

William H. Walker.—The Annealing of Sterling Silver. *American Chemical Society*, Vol. XXIX, pp. 1198–1207.

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[1] In order that the extent of production may be better known, it is designed to publish a list of the publications of the Institute, together with abstracts of the more important papers, arranged alphabetically by departments as follows.

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The metal commonly spoken of as "sterling silver" is an alloy of 92.5 per cent. silver and 7.5 per cent. copper. As is the case with other alloys, sterling silver suffers a change in its physical properties when subjected to mechanical treatment, such as rolling, drawing, stamping, etc.; becoming hard, stiff, and brittle. When the alloy is annealed by heating it to low redness, these undesirable properties, doubtless due to molecular strains, disappear, and the ware then may be subjected to further mechanical treatment. These frequent heatings produce on the alloy a scale of black copper oxide, which so long as the articles were finished by hand was entirely removed by the subsequent filing and buffing necessary to produce the required polished surface. When the more modern methods of rolling and stamping were introduced, a very much less severe treatment on the buffing wheels was necessary to produce the desired polished surface, and consequently the silver was removed to a very much less extent. Under these circumstances there appeared upon the finished ware a dark sheen, or reflex, which greatly diminished the luster and market value of the goods. This undesirable appearance is called by the workmen "fire surface," and is found to penetrate the silver alloy to a distance roughly proportional to the number of times the alloy has been annealed. In order to remove this "fire surface" it is necessary to place the ware in strong nitric acid and dissolve away the alloy until the darkened portion has disappeared. This entails a loss to the manufacturer both from the silver dissolved and the danger of deep pitting due to the irregular action of the nitric acid.

In the investigation here presented, the cause of this "fire surface" is found to be the absorption of oxygen by the silver and the formation of copper oxide within the alloy. A method is provided by which silverware may be annealed and worked without deterioration due to this cause. This method, which is now employed in practically all the large silver-producing factories in America, consists essentially in annealing the ware in an artificial atmosphere, consisting of a mixture of inert gases and reducing gases so proportioned that the reducing gases (for example, hydrogen and carbon monoxide) prevent the penetration of the oxygen present, and the inert gases (carbon dioxide and nitrogen) prevent the deterioration of the silver by the absorption of the reducing gases.

William H. Walker, Anna M. Cederholm, Leavitt N. Bent.—The Corrosion of Iron and Steel. *Journal American Chemical Society*, Vol. XXIX, pp. 1251–1265. September, 1907.

Some time ago an investigation was undertaken with a view to throwing light upon the much discussed question as to whether wrought iron is more resistant to corrosion than steel. To this end a relatively large quantity of pure iron was prepared, and with this as a basis alloys of iron and varying amounts of the different elements occurring in commercial iron and steel were made by melting the constituents in alumina crucibles heated by an electric furnace operating under a high vacuum. In studying the specimens so produced, it early became apparent that a more complete understanding of the factors which occasion corrosion and the conditions under which corrosion proceeds was necessary in order that our results could be intelligently interpreted. A study of the literature on the subject

showed it to be so voluminous and so altogether contradictory that, as a first step in the study of the general subject of the influence of the constituents of iron or steel upon its corrosion, the mechanism of the reactions by reason of which corrosion takes place was investigated.

The theory of corrosion generally held and most frequently given in text-books is to the effect that iron will corrode only in the presence of liquid water, oxygen, and carbon dioxide. Dr. W. R. Whitney, while at the Institute, enunciated a theory based upon Nernst's conception of electromotive force and the modern theory of solutions. He pointed out that corrosion is an electrochemical phenomenon, depending only upon the difference of potential between two points and the resistance in the circuit. Iron dissolves in water free from both oxygen and carbon dioxide because the solution-pressure of iron is greater than that of hydrogen, in a way analogous to the well-known precipitation of copper from a copper sulphate solution by iron, the latter being dissolved. Hence acidic reagents, even carbon dioxide, which increase the concentration of the hydrogen ion will accelerate corrosion, and, on the other hand, reagents which decrease the concentration of the hydrogen ion (as, for example, the alkalis or any salts which by hydrolysis produce hydroxyl ions) will inhibit corrosion.

A number of investigators, in repeating Whitney's work, have failed to duplicate his results; and the electrochemical theory has not been generally accepted, if one may judge by references to the subject made in modern text-books. The work of this laboratory shows that Whitney was entirely correct in his conclusions, although he omitted one important factor, namely, oxygen. It has been shown that iron does dissolve in water free from oxygen and carbon dioxide, but only to a limited extent. Action ceases when the cathodic portions of the iron become polarized by the separated hydrogen, and continues only when this polarizing hydrogen is removed. As a corollary of this, it has been found that the speed of corrosion of iron in water is a linear function of the partial pressure of the oxygen in the atmosphere above it. Experiments have been devised in which the necessity of this depolarization, in order that corrosion may continue, is easily and convincingly shown.

As a result of this work we have:

(1) Proven again that carbon dioxide is not essential for the corrosion of iron;

(2) Substantiated the work of Whitney and shown that iron does dissolve in the absence of carbon dioxide and oxygen;

(3) Shown that the primary function of oxygen in the corrosion of iron is in depolarizing those cathodic portions of the iron upon which hydrogen tends to precipitate, and that a secondary function is the oxidation of the ferrous iron ion to the ferric form, with its subsequent precipitation as ferric hydroxide;

(4) Shown that the rapidity of corrosion in water is a linear function of the partial pressure of the oxygen in the atmosphere above the water;

(5) Shown that an electric current can pass between bright iron and iron covered with scale, (1) if the concentration of the hydrogen ions be increased by the presence of an acid or (2) if oxygen or some other depolarizing substance be present.

(6) Shown that in certain instances areas having marked difference in potential

exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion.

William H. Walker and *Colby Dill.*—The Influence of Stress upon the Corrosion of Iron. *Proceedings of American Society for Testing Materials*, Vol. VII, pp. 229–243. December, 1907.

The influence of stress upon the corrosion of iron and steel is a subject which has received a great deal of attention during the last few years, but which, notwithstanding the work which has been published upon it, has remained unsettled. The fact that in riveted sheet-iron work the rivets and the plate often show a marked difference in their rate of corrosion has been frequently noted. Portions of bridge members sometimes show a selective corrosion. The barbs of the so-called barbed-wire fencing generally corrode more rapidly than do the main wires. The differences in corrosion have been explained by some writers of repute as due to a difference in potential set up in the two members by the unequal strain to which they are subjected. By others this is denied. The present investigation was undertaken with the hope of throwing some light upon the question of the sign and magnitude of the potential changes caused by straining a piece of iron, particularly below the elastic limit, and therefore of the change in the tendency of strained iron to corrode. From theoretical considerations the increase in potential which a bar of soft iron suffers when strained to its elastic limit is shown to be very small—but a fraction of a millivolt. A series of experiments carried on with great care confirms this prediction and proves that, notwithstanding a rapid increase in the difference of potential while the stress is being applied, which difference disappears when the machine producing the stress is at rest, there is brought about no condition which materially influences corrosion.

The results of the foregoing experiments may be summarized as follows:

1. The magnitude of the potential changes suffered by soft iron when tested in a tension machine below the elastic limit is exceedingly small. In the majority of cases it was less than 0.0001 volt. The maximum change was 0.0004 volt. This change can have no appreciable effect upon corrosion.

2. The change when great enough to be measured was negative, *i. e.*, the strained metal had a slightly less tendency to corrode than the same metal unstrained.

3. Somewhere above the elastic limit the potential rises suddenly several hundredths of a volt. The magnitude of the increase depends upon the rate of straining and ceases abruptly when the straining ceases.

4. Measurements upon specimens under torsional stress give results similar to those obtained from tension tests.

5. Out of a considerable number of specimens strained to breaking the potential of six reached a constant value shortly after fracture. The difference between he initial and final potentials varied from 0.0019 volt to 0.0077 volt.

We conclude, therefore, that even beyond the elastic limit the corrosion of is not greatly affected by stress.

Civil Engineering

George F. Swain.—Report to Massachusetts Railroad Commission on Railroad Bridges and Street Railway Bridges. In *Report of Railroad Commission to Legislature.*

Electrical Engineering

Dugald C. Jackson.—College and Apprentice Training. *Proceedings American Society of Mechanical Engineers,* Vol. XXIX, pp. 394–396. November, 1907.

Discussion of paper by J. P. Jackson, read before the American Society of Mechanical Engineers.

Dugald C. Jackson, William H. Crumbs, and *George W. Wilder.*—Report on the Telephone Situation in the City of Chicago; in Respect to Service, Rates, Regulation of Rates, etc. By a Special Commission. April 3, 1907. 124 p. 4to.

Geology

Charles H. Clapp.—The Clays of North Dakota. *Economic Geology,* Vol. II, pp. 551–564. September–October, 1907.*

The Fourth Biennial Report of the State Geological Survey of North Dakota is a report on the clays and clay industries of that state and is based on two years' field laboratory work by Mr. C. H. Clapp, and on the previous work of Professor Babcock, of the University of North Dakota, and Dr. Leonard, state geologist of North Dakota.

The contents of the report are as follows:

Part I.—Clay and its Properties, with Special Reference to North Dakota Clays.

Part II.—Stratigraphy of North Dakota Clays.

Part III.—Economic Geology of North Dakota Clays.

Part IV.—Uses and Value of North Dakota Clays.

Part V.—Methods of Brick Manufacture and Description of the North Dakota Industry.

William Harmon Niles.—Address at the Celebration of the One Hundredth Anniversary of the Birth of Louis Agassiz. *Proceedings of the Cambridge Historical Society,* Vol. XI, pp. 91–96. October, 1907.

In my address I gave a personal reminiscence of my acquaintance with Pro-

fessor Agassiz as a student in his laboratory from 1862 to the time of my graduation in 1866. I gave some account of his method of testing applicants for their interest in natural history and of his method of training his students to become professional naturalists. I spoke of the impression produced upon me by his remarkable power of observation, and gave some instances of which I was a personal witness.

I also spoke of his wonderful memory as united with this power of observation. Referring to the fact that there are 418 different titles of his writings in science, I mentioned but few of them, among them his noted work on Fossil Fishes and his work on Glaciers; and mention was made of his teaching the evidences of Glacial Action in this country.

I recalled to memory his joy over a letter from Sir Roderick Murcheson, in which at last his glacial theory was accepted.

I spoke of his great work in founding the Museum of Comparative Zoölogy in Cambridge, its wonderful collections, and the numerous men of science who received their instruction from him.

Hervey W. Shimer.—Geology of Connecticut (Book Review). *Technology Quarterly,* Vol. XX, p. 375. September, 1907.

Reviews Bulletin 6 (Connecticut State Geological and Natural History Survey) —a "Manual of the Geology of Connecticut," by Professors W. N. Rice and H. E. Gregory; and Bulletin 7—a "Preliminary Geological Map of Connecticut," by Professor H. E. Gregory and Dr. H. H. Robinson.

Hervey W. Shimer.—The Broader Features of the Geologic History of North America in Diagram. *Technology Quarterly,* Vol. XX, p. 287.

The article follows T. C. Chamberlin regarding the alternation of subsidence and reëlevation of the earth's crust with the formation and disappearance of epicontinental seas, giving an alternate increase and decrease in the amount of CO_2 in the atmosphere; in the sea an alternation of great limestone beds with those of clastic origin. These considerations are made the basis of a diagrammatic history of the North American continent.

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Davis R. Dewey.—National Problems, 1885–1897. The American Nation, edited by A. B. Hart, Vol. XXIV. New York: Harper, 1907.

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Gaetano Lanza.—Report of the Committee on Standard Methods of Tests. Committee V. *loc. cit.* Vol. VII, pp. 150–156. Philadelphia, 1907.

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Walter S. Leland and *H. A. Everett.*—Service Test on Steamship *Governor Cobb* (Parson's Turbine).[1] *Trans. Society Naval Architects and Marine Engineers,* November, 1907. Vol. XV.

C. H. Peabody.—Thermodynamics of the Steam Engine. Edition 5. New York: Wiley, 1907. 533 pp.

C. H. Peabody.—Tables of the Properties of Steam and Other Vapors and Temperature-Entropy Table. Edition 7. New York: Wiley, 1907. 5 + 131 pp., 8vo.

Physics

D. F. Comstock.—The Relation of Mass to Energy. *Philosophical Magazine,* January, 1908.

If a piece of matter be considered as an electrical system, possessing any structure or internal motions, but having on the whole a kind of average symmetry, then it may be shown that the electromagnetic mass of such a system for ordinary velocities is given by

$$\text{Mass} = \frac{4}{3}\frac{1}{V^2}E$$

where V is the velocity of light and E is the total electromagnetic energy of the system. Thus the mass of the system is determined solely by its energy content, and the idea is suggested that mass and energy may have something in common. This result has several interesting implications.

Any reaction which is caused by the action of electric forces will involve a change in the electromagnetic energy content of the system, and hence according to the above view will be accompanied by a change of mass. This change will, of course, in general be a decrease. In the case of ordinary chemical reactions calculation shows that this change would be too small to be detected, but in the case of radioactivity, where the energy lost is relatively much greater, a sensible change is to be expected. Thus on this view the atomic weight of the various products of radium cannot be accurately calculated from the number of α-particles lost, for there is this further decrease in mass due to the loss of energy.

[1] To be reprinted in the June number of the Quarterly.

The evolutionary theory of the elements has always met an almost insuperable difficulty in the fact that there appears to be no *exact* regularity of any kind throughout the list of atomic weights.

Some years ago Rydberg came to the conclusion that it was necessary to consider the atomic weights, up to that of iron, as made up of two distinct parts, $N + D$, where D is a very small difference, a slight deviation in fact from (N). Exact harmonious relations exist between the various N's, and Rydberg seems to consider the D's as representing real physical deviations and not merely mathematical remainders.

From the point of view of loss of mass accompanying energy dissipation, it is evident that these small irregularities are just what is to be expected.

Finally it is to be noticed that if for all matter the ratio of mass to weight is sensibly the same, the above mentioned proportionality between mass and included energy can only imply that the gravitation of a body is always proportional to its total energy content, and this constant proportionality seems to point toward the conclusion that it is confined energy which gravitates and not mass in any other sense.

It is perhaps well tc point out that the conclusion respecting gravitation involves the assumption that all the mass of matter is electromagnetic, while the conclusion respecting loss of mass and atomic weight irregularities requires only that the forces causing the energy change be electric or magnetic, *i. e.*, requires only that *part* of the total mass be of electromagnetic origin.—*Science,* N. S. Vol. 26, No. 669, Oct. 25, 1907.

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TECHNOLOGY QUARTERLY

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Vol. XXI JUNE, 1908 No. 2

RECENT DEVELOPMENTS IN FIRE PROTECTION DEVICES

By GORHAM DANA

Read March 12, 1908

THE importance of fire protection engineering is perhaps best realized when we consider the annual fire waste of the country. In 1875 this was about $78,000,000; in 1885, $102,000,000; 1895, $142,000,000; 1905, $165,000,000; 1906 (the year of the San Francisco earthquake), $500,000,000. The figures for 1907 are estimated at $180,000,000, which is perhaps a fair average for the last few years.

America stands first in the list of countries in the amount of property annually destroyed by the fire fiend, and it is natural, therefore, we should stand first in the modern crusade against this destructive element. Figures showing the amount of money annually spent for this purpose would be extremely interesting, but they are difficult to obtain. They would include the cost of maintaining fire departments in all cities and towns; the cost of enforcing building laws, maintaining fire marshal departments, equipping and maintaining testing laboratories; the expense of insurance companies, with their numerous ramifications of inspection bureaus, rating organizations, etc.; part of the expense of ordinary water works systems; and lastly, the cost of equipping buildings with modern fire appliances.

First of all it should be realized that this fire waste constitutes an absolute destruction of property, $180,000,000 worth of property completely wiped out of existence every year.

It is often said that insurance companies pay the loss, if happily the loser is fully insured; but it is not always realized that insurance companies simply distribute the loss among many persons, but do not really pay it. They are nothing but banking institutions, receiving money from many and distributing it among a few. You and I, and every one who insures, are really the ones who pay the losses.

With this stupendous and constantly growing ash heap threatening our progress, it behooves every citizen to make himself familiar with the conditions and do his part toward improvement. No one would claim that the conditions cannot be improved, but few are sufficiently versed to know just what should be done. It is here that science is appealed to, as in so many of the practical problems, for a solution of the difficulty.

Modern fire fighting appliances, as used by fire departments, have already reached a high state of usefulness, but they are certainly not keeping pace with modern building construction. The recent fire in the Parker Building, in New York, is an excellent illustration of this fact. Here was a building of modern fire-resisting construction, twelve stories in height, located in the heart of the city. It was built for an office building but used as a printing establishment, and contained a large amount of combustible material. While this, no doubt, had something to do with the heavy loss, still the fact remains that after the fire had gained headway the firemen were powerless to cope with it, and it practically burnt itself out. Hose streams were utterly useless above the eighth story, and still this was in the heart of the largest city in the country, where the fire department is supposed to be second to none. With this condition of affairs in a twelve-story building, what are we to expect in the twenty, thirty, and forty-two story buildings of our large cities? It is only a matter of getting enough combustible material into these buildings at a high elevation, and enough of these buildings close together, and the conditions are ripe for an aërial conflagration where the modern fire department would be as helpless as in attempting to quench an eruption of Vesuvius.

Under such conditions the fire protection engineer is sought for advice. He is the product of the last quarter century, but his work is no less important than that of the older branches of engineering. Nearly all of the technical schools are turning out men to enter this profession, and their numbers are constantly increasing. In the city of Boston alone there are probably over one hundred such engineers. A fire protection engineer is usually found in the employ of the insurance interests, for

insurance companies have long since found it necessary to devote their attention to the lessening of fires. While they can adjust rates to cover any conditions, it is clearly for their interests in the long run, as well as that of the community at large, that the fire losses should be kept as small as possible. Their work may be briefly summed up as follows:

First, the investigation of methods of preventing fires; second, devising and supervising means of extinguishing them with as little loss as possible. The method of preventing fires we will not deal with at length. Suffice it to say that it is done by constant inspection of existing conditions, study of fires as they occur, and an effort to eliminate such conditions as favor the starting of fires.

Coming to the second point, the duties of the insurance engineer are principally along the lines of private fire protection, for it is believed that by getting improvements in individual plants, thus lessening the chance of a fire of large proportions, more can be accomplished than by endeavoring to produce appliances that will extinguish conflagrations. A fire in its incipiency is always easily extinguished, and by the aid of appliances that will give prompt alarm or bring the extinguishing agent into quickest use the greatest hope lies. It is perfectly possible to prevent such conflagrations as that in Baltimore, with its $50,000,000 loss, and the one in San Francisco, with its loss of $350,000,000, if the public would coöperate with the fire protection engineer. The remedy may be expensive, but it is certainly worth the money it costs.

These preliminary remarks may be enough to emphasize the importance of modern fire protection devices.

Historical Data

The first fire engine of which we have record was mentioned by Hero, 150 B.C. Such devices were, however, not used to any extent until about the seventeenth century. "Hand squirts" were first used in London about 1600, and flexible hose was introduced about 1672. Steam fire engines were invented in London about 1830, and first used in this country about 1853.

The first attempts at private fire appliances were along the lines of fire pails, and these, by the way, are even today considered of the greatest value. The larger manufacturing plants often installed steam pumps, which could be used to feed standpipes in the mills or hydrants outside. These were single cylinder pumps of the capacity of 200 to 500

gallons per minute, and gave very fair results if properly cared for and intelligently handled.

About the year 1870 perforated pipes began to be used. This form of protection consisted of a series of pipes running along the ceiling, located 8 to 12 feet apart and containing a series of small holes. These holes were so located that when the water was turned on a number of jets were thrown close to the ceiling, dropping to the floor below and wetting it more or less thoroughly. The piping on each floor was operated by a valve located outside the building, or in some other suitable location. In case of fire the proper valve was opened, provided some one was fortunate enough to be on the spot at the right time. This crude device gave very poor distribution as compared with modern sprinkler systems, and also had the defect of wetting down a much larger area than that covered by the fire. The holes also became readily clogged by dirt and corrosion.

AUTOMATIC SPRINKLERS

Automatic devices for the extinguishing of fires were not installed in a commercial way until about 1878, although experimental devices were made as early as 1864 and patents were issued much earlier. In 1806 John Cary patented a device consisting of "Rose" sprinklers, supplied by an elevated tank of water and controlled by a weighted valve which was operated by the burning of cords.

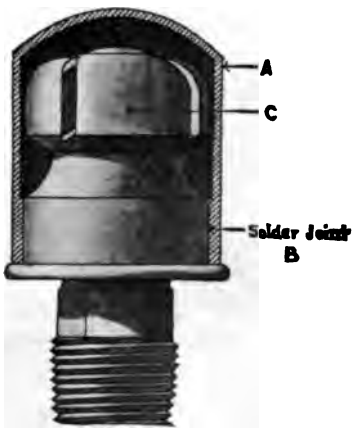

FIG. 1. — PARMELEE SPRINKLER
(Cap in Section)

"Water joint" type. The cap *A* is soldered at the point *B* and is full of water. The turbine *C* distributes the water when the head fuses and opens.

The first sprinkler head to be used commercially was the "Parmelee" (Fig. 1). This consisted of a revolving cylinder or turbine, containing slits through which the water could issue, the whole being covered by a cap which was soldered in place. The sprinklers were located about every 10 feet apart throughout the building, or the hazardous sections of the building, at a distance of 4 or 5 inches below the ceiling. They were connected to a system of piping which was kept full of water, fed by an

elevated tank, public water supply, or some other reliable source. Heat from a fire would fuse the solder, allowing the sprinklers to open and extinguish the fire. The solder melted about 160° F., which is the same melting point as is used today; but the head lacked sensitiveness for the reason that the solder joint was not insulated in any way from the long line of piping and the water was in direct contact with the joint.

It might be stated here that 155 to 160° is as low a melting point as is practical for solder. The formula is approximately as follows: bismuth, 4 parts; lead, 2 parts; cadmium, 1 part; tin, 1 part. This formula is based on patents granted Barnabas Wood in 1860.

Sir Isaac Newton in 1799 discovered that certain alloys melted lower than their constituents. The melting points of some of the component parts are as follows: bismuth, 476°; lead, 504°; tin, 421°.

Any solder melting at a lower temperature contains mercury, which deteriorates with age. Furthermore, this temperature is considered low enough; solder fusing much lower than this is liable to give way in very hot weather. When repeatedly heated nearly to its melting point, solder is subject to cold flowage, especially if under strain. For this reason it is considered wise to allow a leeway of about 50° F. between the highest temperature to which the room is subjected and the melting point of the solder used at that location. In dry rooms and other places where high temperatures are found a higher fusing solder is used; the common types found on the market melt respectively at 212, 286, and 360° F.

The rules for the installation of automatic sprinklers cover forty-three pages and are becoming more complicated all the time. Still, in the important features they have changed but little since the early installations. The rules for spacing state that heads shall be located not over 10 feet apart under smooth ceiling and not over 12 feet apart in 8-foot bays or less. In other words, one head is supposed to cover an area not exceeding 100 square feet. In the matter of pipe sizes, there have been more changes. In the early equipments, one head was allowed to be fed by a ¾-inch pipe; three heads by a 1-inch pipe; six heads by a 1¼-inch pipe; ten heads by a 1½-inch pipe, etc. Under the present rules, one head is allowed on a ¾-inch pipe; two heads on a 1-inch pipe; three heads on 1¼-inch pipe; five heads on 1½-inch pipe, etc.

Piping is supported from the ceiling at an elevation such that the deflectors of the sprinklers shall be between 3 and 10 inches below the bottom of the joists or surface of the ceiling. The heads are arranged to cover every nook and corner, so that a fire cannot start at any point

without having a sprinkler head within 5 feet of that point (measured horizontally) ready to open when heated to the proper temperature.

Amongst the early sprinklers may be mentioned the Brown, Burritt, and Bishop, all being of a type somewhat similar to the Parmelee.

The next step in advance was the removal of the solder joint from contact with the water, thus making the head more sensitive. The Brown,

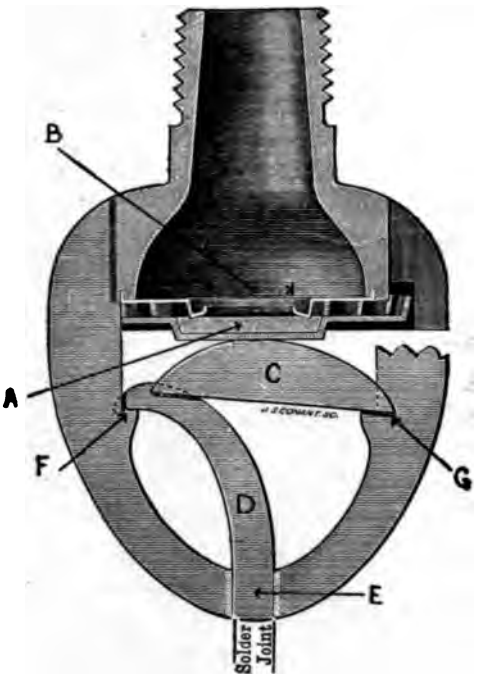

FIG. 2.—GRINNELL "METAL SEAT" SPRINKLER
(Sectional View)

The valve *A* is held against the outlet *B* by the levers *C* and *D*. The solder joint is at *E*. The valve seat and deflector are all one piece, and when the head fuses this falls as far as the notches *F* and *G*, on which the levers rest.

Burritt, and Bishop heads were all developed along these lines, but the Parmelee was superseded by the Grinnell (Fig. 2). This latter is perhaps the most interesting of all sprinklers, for it is the one having the largest sale here and abroad, and is installed by the largest sprinkler company. In fact, the inventor, the late Frederick Grinnell, was the most important factor in the sprinkler business in America. Starting in the steam fitting business, he became interested in sprinklers, and at first installed the Parmelee head. About 1882 he first put out the Grinnell head. This

was probably the first sprinkler to use a splash plate or deflector for distributing the water, and it contained many other novel features, including a flexible diaphragm, lead disks, etc. This sprinkler later developed trouble by sticking at the valve, and three other types followed between 1884 and 1890. In the second, a block-tin disk was used. In the third, the same disk was used, but the seat ring was narrowed. In the fourth, a babbitt disk was used.

Other sprinklers used about this time were the Kane, of which there

FIG. 3. — GRINNELL "GLASS DISK" SPRINKLER
(Sectional View)

The glass disk, or button, closes the outlet which is in a thin metal sheet. The glass disk is held in place by the vertical strut composed of three pieces of metal soldered together. This strut falls away when melted, allowing glass disk to be pushed out by the water, which then strikes the toothed deflector and is properly distributed.

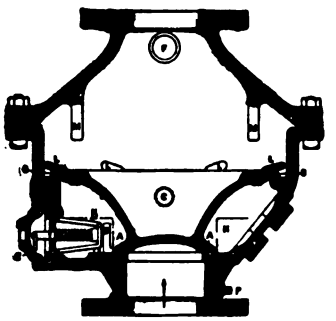

FIG. 4. — OLD GRINNELL DRY VALVE
(Sectional View)

The movable valve *LLAA* has an air seat at *BB* and a water seat at *AA*. The intermediate space *K* is not under pressure. The air seat is about eight times the area of the water seat, so that one pound of air will hold back about eight pounds of water. The latch *E* holds the valve open after it has tripped and prevents water columning.

are many types; the Neracher, which is now controlled by the General Fire Extinguisher Company; the Ruthenburg; and the Walworth.

In the original Walworth head, the movable arm was soldered to the frame, but later the arm was held by a fusible link, which made it much more sensitive.

About the year 1890, further improvements were made in sprinkler construction, and it is from this time that the general type used today may be said to date. The Grinnell glass disk head (Fig. 3) appeared in 1890; International the same year; Manufacturers', 1893; Hibbard, 1894.

In the Grinnell glass disk head the seat is of glass, thus effectually preventing corrosion at this point. The valve is held closed by a strut built up of three sections soldered together, a great improvement over the old lever type of support. The head was smaller and greatly improved in appearance over the earlier types.

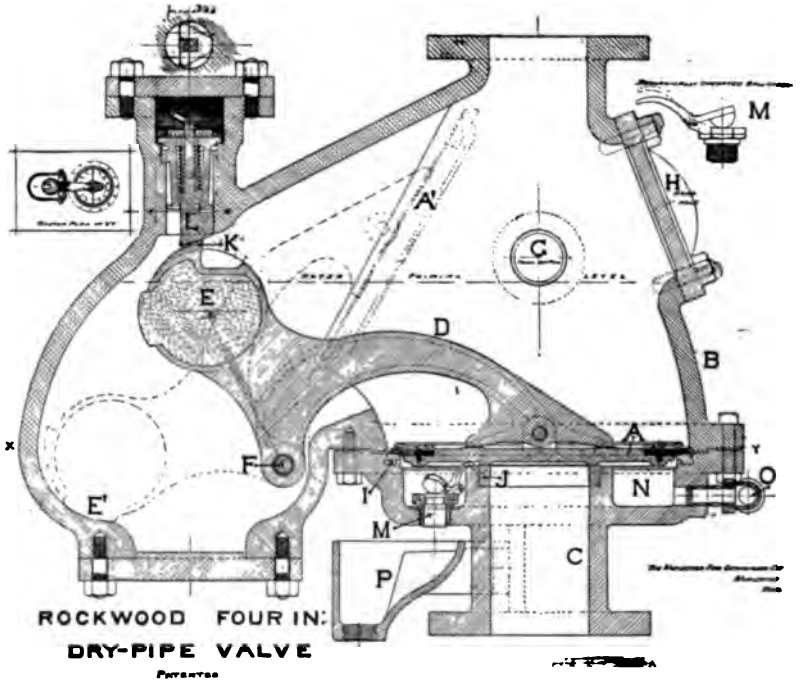

FIG. 5. — ROCKWOOD DRY VALVE
(Sectional View)

The valve *A* is attached to an arm *D* pivoted at *F*. It has an air seat near *I* and a water seat near *J*, the former being about eight times the area of the latter. *H* is a removable hand plate and *L* is a latch to prevent the valve from seating after it has opened.

Since 1890 there have been numerous improvements in details, but the general principles involved remain practically unchanged.

There have been some 363 patents issued on sprinklers in the United States, and a large number have been built that were never patented. Of all this vast array, only seven remain on the list approved by the National Board of Fire Underwriters today.

The modern sprinkler head is a well-developed device and very reliable in its action. Further developments may come, but it does not seem likely

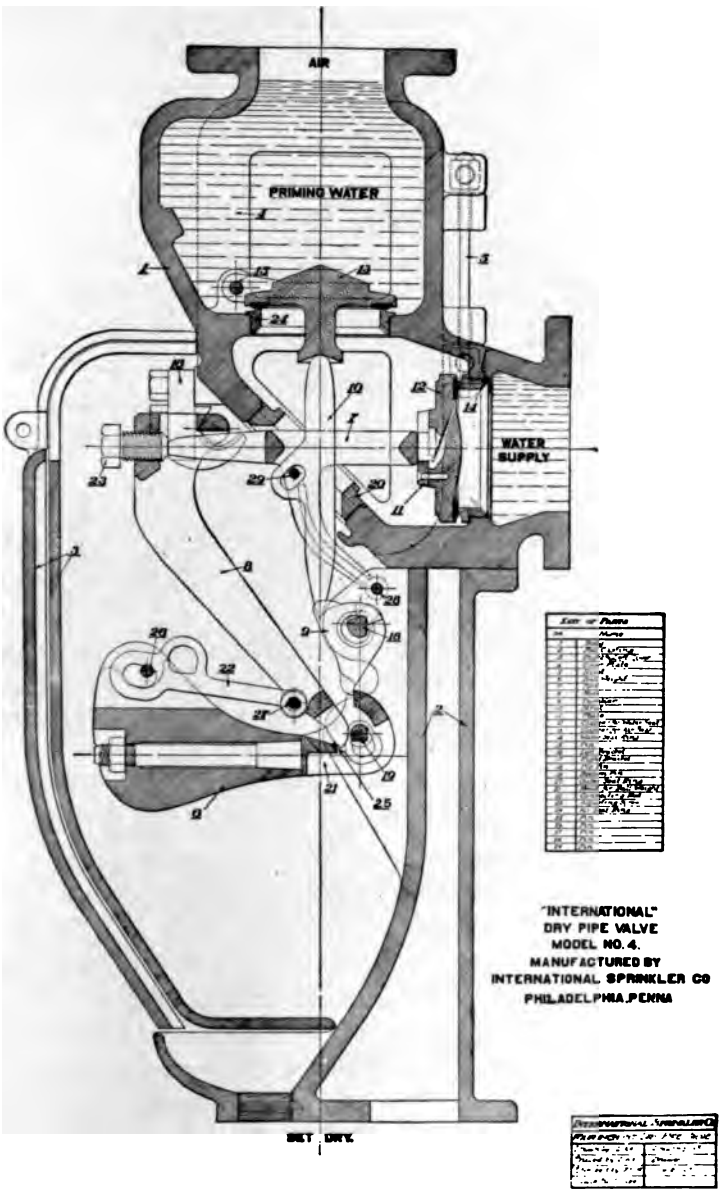

FIG. 6. — INTERNATIONAL DRY VALVE
(Sectional View)

The water valve 11 is held in place by a series of struts and levers 7, 8, 6, 9, and 10 bearing finally on the air valve 13. This leverage gives a differential of about 6 to 1 between the air and water seats. A little priming water is shown above the air valve in order to give a tighter joint.

that they will be of a radical nature. It will not corrode under ordinary conditions, that is, where no acids are present; and it will open as it is designed to do when heated to the proper temperature.

The amount of water delivered under different pressures may be of interest. The modern sprinkler has an outlet of ½-inch diameter and will discharge approximately the following:

Under	5 pounds	pressure	12 gallons per minute
Under	15 pounds	pressure	21 gallons per minute
Under	30 pounds	pressure	30 gallons per minute
Under	75 pounds	pressure	50 gallons per minute
Under	100 pounds	pressure	58 gallons per minute

Dry Valves

Sprinklers are often installed in buildings where there is no heat and where the water in the pipes would freeze. In the early stages of sprinkler protection, the dry valve was invented for this contingency, and it is now a very important factor. There are several approved designs, but the main idea in each is to supply a mechanism for holding back the water by means of compressed air under a lighter pressure than the water. Of course it is perfectly possible to install an ordinary swing check valve and pump a heavier air pressure above it than there is water pressure below. The trouble with this scheme is that it is difficult to maintain piping tight under an air pressure of 100 or 150 pounds, and furthermore it takes too long to let this air pressure out of the pipes after a sprinkler head has opened. The rush of air fans the fire, and the time when the water can reach the outlet is greatly delayed.

The simplest form of dry valve, the old Grinnell (Fig. 4), is a differential check valve. The upper or air seat is about eight times the area of the lower or water seat, and between the two is an intermediate space which is not under pressure. This intermediate space is used to actuate the alarm-giving device when the valve opens. A later development of this idea is found in the Rockwood dry valve (Fig. 5), where the valve is compressed into a single disk with two seats, and the whole placed on an arm which swings entirely out of the water way when open.

In the International valve (Fig. 6) we have the water seat held closed by a system of levers, and in the Manufacturers' valve (Fig. 7) a somewhat similar arrangement.

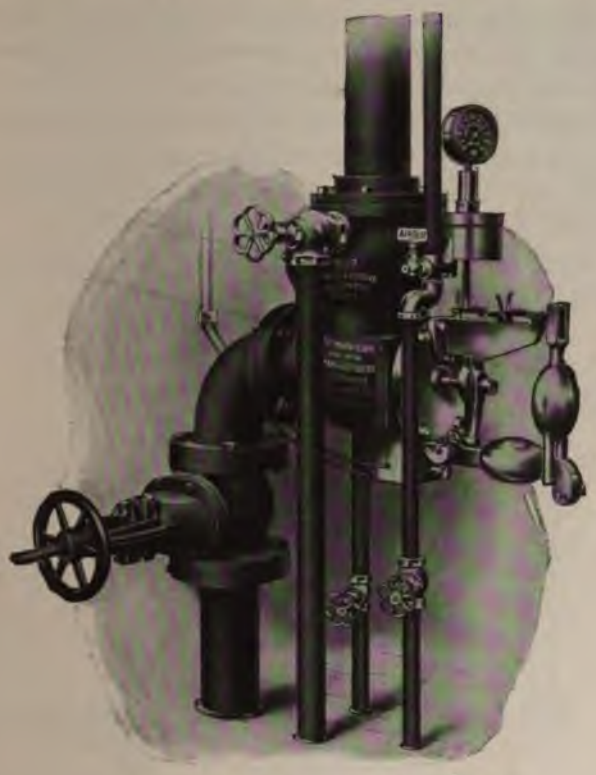

FIG. 7. — MANUFACTURERS' DRY VALVE
(Exterior View)

This valve has a separate water and air seat. The water seat is held in place by a system of levers and weights which bear finally on a piston in the chamber below the gage. This piston is held down by air pressure piped from the system on the floor above.

ALARM VALVES

Early in the art of sprinkler protection it was found that some form of alarm device was very desirable in a sprinkler system. Such a device will prevent a sprinkler system from doing a heavy water damage, as, for instance, in case a sprinkler should be opened by fire, and the fire extinguished by it when no one was in the building. There have been many cases where this has happened or where a sprinkler operated from some other cause, and where the trouble was not discovered until the system had been running for many hours. Where there was a dry valve, it was easy to arrange an alarm connected to this. For instance, the filling of the intermediate space in a Grinnell dry valve could be utilized

to make an electrical contact as well as to ring a rotary gong run by water power. Where there is a wet pipe system a separate alarm valve is required for this purpose. The early types consisted of ordinary check valves with a packed stem extending through the casing and connected by an arm to some form of electric contact-closing device.

The trouble with these was twofold. First, the possible sticking at the packed stem; and second, the danger of false alarms due to water hammer. These defects have been practically solved in the modern approved valves, the Grinnell and the International (Figs. 8 and 9).

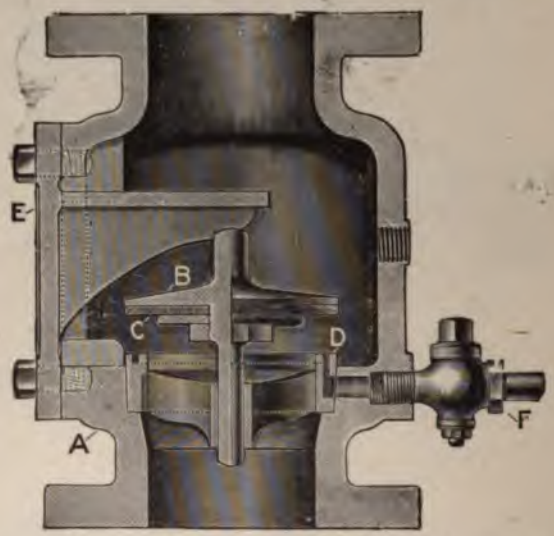

FIG. 8.—GRINNELL "VARIABLE PRESSURE" ALARM VALVE
(Sectional View)

The vertical check valve *B* bears when closed on a grooved seat *D* and closes the groove. When it opens, the water passes into the groove and hence through pipe *F* and interrupting pot to electric circuit closer or water motor gong (not shown).

WATER SUPPLY

Let us now consider the water supplies for these systems. The insurance rules always require two separate sources of water supply for minimum rate, for it often happens that one supply will become crippled. Thus, street mains may break, tanks may be drained by leaks, and pumps may break down. A reliable system of water works is usually the most satisfactory source of supply, provided the pressure is sufficient. This pressure should be such as to give at least fifteen pounds at the highest point in the system.

Gravity Tanks are used very commonly as a source of supply. Formerly, a 5,000 gallon tank at an elevation of 12 feet above the roof

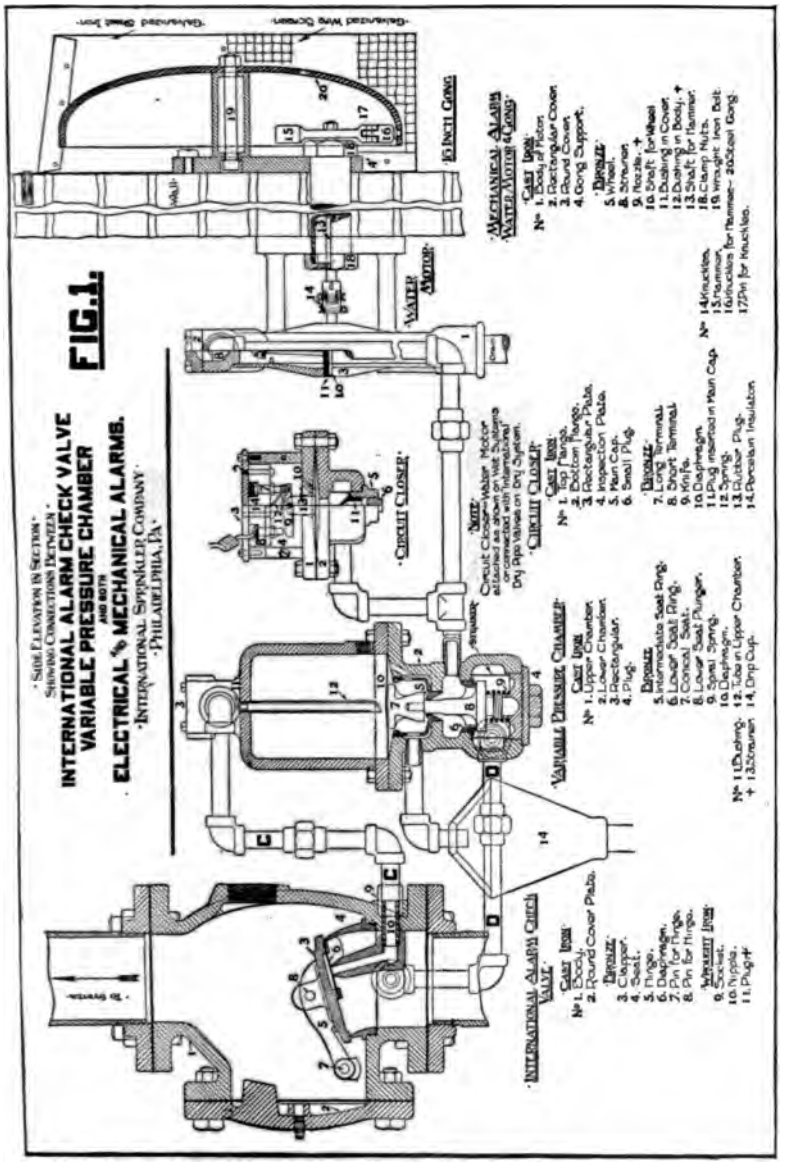

FIG. 9. — INTERNATIONAL ALARM VALVE
(Sectional View)

The swing check valve 3 tightly closes the outlet of pipe *C* when on its seat. When the check opens, water flows through pipe *C* to variable pressure chamber, hence to electric circuit closer and water motor.

was considered a satisfactory supply for moderate sized buildings, but today the usual size is 10,000 to 15,000 gallons, with an elevation of 15

to 20 feet. Flat iron hoops were formerly used, but round painted hoops are the standard today. In large plants, tanks as large as 200,000 gallons are installed at elevation up to 200 feet. These large tanks are of steel, on trestles of the same material. In Charlestown there is a tank of 100,000 gallons, on a 200-foot trestle, feeding sprinklers in the Boston & Maine grain elevator. The top of the tank is higher above ground level than is Bunker Hill Monument above the level of the hill. Concrete tanks are also being installed to some extent, and they have the advantage of cheap maintenance. A firm in Boston is now building two concrete tanks, one being 50,000 gallons' capacity on a 100-foot trestle, and the other 100,000 gallons on a 150-foot trestle.

Pressure Tanks are occasionally used, especially where the other source of supply is under light pressure. These are built of boiler iron, with joints tightly caulked to withstand a heavy pressure. They are filled two-thirds full of water and then sufficient air is pumped in so that when the last water is being discharged from the tank it will give a pressure of fifteen pounds at the top of the building. This means a pressure of seventy-five pounds if the tank is at the roof level, and a higher pressure if it is at a lower level.

These tanks have been used for about twenty-five years, and there has been but little development except in size. The early ones had a capacity of 2,000 to 4,500 gallons, while today tanks of 7,500 and 9,000 gallons are being installed. The Macy Department Store in New York has a complete sprinkler system of over 11,000 heads, supplied by six 10,000-gallon gravity tanks and six 6,000-gallon pressure tanks.

Steam Pumps.—Pumps are also a common source of supply, and there has been a striking development in these devices in the last twenty-five years. The old steam pumps were single cylinder affairs, poorly designed to deliver a large volume of water at short notice after lying idle for many months. The modern Underwriter steam pump is designed especially for fire service, with bronze pistons and plungers, stuffing boxes, brass-lined, large area valves, large steam and exhaust passages, large suction, wrought iron side levers, etc. As a part of the pump are required capacity plate, gauges, vacuum chamber, relief valve, priming pipe, hose valves, etc.

Automatic regulators are frequently required with steam pumps, and these, too, have undergone a radical development. The type most used was practically designed by an insurance engineer, and is particularly fitted for fire pump work.

Rotary Pumps.—Rotary pumps are frequently used for fire protection, especially where there is plenty of water power and little or no steam available. In the older types there was an undue opportunity for corrosion, large friction loss, considerable variation in pressure, and other undesirable features. In the National Standard Rotary pump, the specifications for which were only recently drawn up by a committee of the National Fire Protection Association, these defects have been

FIG. 10.—A. D. T. CO. GATE VALVE ATTACHMENT

c = case; *d* = case contact; *e* = rubber roller; *ff* = German silver springs; *g* = post for closing case contact.

This is designed to attach to a gate valve so as to give an alarm as soon as any one starts to close the valve.

largely eliminated and numerous attachments, such as air chamber gauges, hose connections, etc., are included in the requirements.

Other Pumps.—Electrically driven pumps, both of the plunger and rotary types, are occasionally used, and specifications have been made covering all details of these. Within a very few years centrifugal or turbine pumps have been built for fire purposes, but the insurance interests have not yet promulgated any specifications for their construction. They are, however, extremely well adapted for electric driving where the suction is under a head, and they will, undoubtedly, be a considerable factor in the future.

Sprinkler Supervision

Automatic sprinkler protection has become so highly developed that very few fires in buildings so equipped are not properly controlled. There are occasionally failures, but these are almost always due to one of the following causes:

1. Gate valve on system closed.

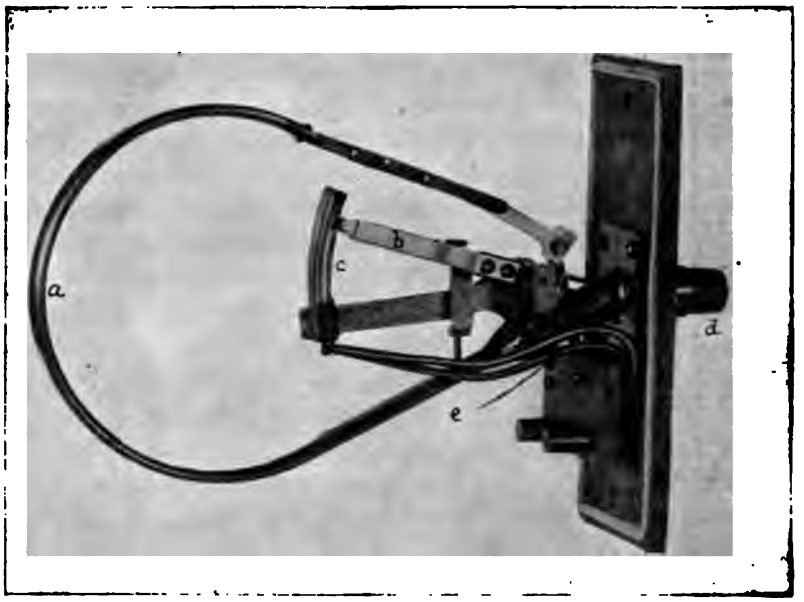

Fig. 11.—A. D. T. System, Pressure Device

a = Bourdon spring; *b* = lever operating Bourdon spring; *c* = contact springs; *d* = pipe connection to pressure tank or dry system. This is designed to be attached to a pressure tank or dry sprinkler system and to give an alarm if pressure falls below a predetermined point.

2. Water supply out of commission, due to empty tanks, crippled pumps, or freeze up.

To reduce these sources of failure to a minimum, sprinkler supervisory systems have recently been placed on the market.

The object is to connect all gate valves, alarm valves, tanks, etc., with electric circuits running to a central station, and so arranged that as soon as a valve is closed, the water in a tank becomes too low, or the temperature in a tank nears freezing point, etc., an alarm is transmitted.

To accomplish this, a closed circuit system is used, all wiring in the

building being in conduit, so that it cannot be tampered with. This conduit runs direct to a circuit breaker fastened to each valve and adjusted so that when the valve is turned more than a specified amount the circuit is broken and an alarm is transmitted.

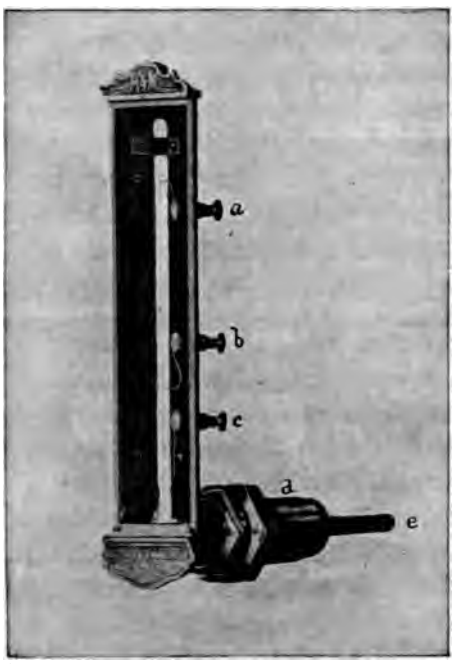

FIG. 12. — A. D. T. TEMPERATURE DEVICE

a = high temperature contact binding post; *b* = low temperature binding post; *c* = constant binding post.

This is designed to attach to a gravity tank to give an alarm in case pressure nears boiling point or freezing point.

In a similar way floats and thermometers are attached to gravity tanks, pressure gauges to pressure tanks, etc., and the whole is arranged so as to be practically tamper proof.

Men are kept on duty at the central station, and in case an alarm is received, a runner is dispatched to investigate the trouble and remain until conditions are restored to normal, if circumstances require it.

With such a system properly installed and maintained, the chance for failures in sprinkler systems will be small.

STATISTICS

Before leaving the subject of automatic sprinklers it might be interesting to consider some statistics.

In the city of Boston there are 175 buildings equipped with sprinklers. In 1906 there were thirty fires in these buildings, entailing a loss of $5,723, or less than $200 per fire.

In New England there are probably between 3,000 and 4,000 plants equipped, some being large mills covering many buildings.

The National Fire Protection Association statistics for ten years, covering over 5,000 fires in buildings equipped with sprinklers, show that 74.5 per cent. of the fires operated eight sprinklers or less, and that 93 per cent. of the fires were extinguished or properly held in check by sprinklers.

The General Fire Extinguisher Company, of Providence, has installed over 10,000,000 sprinkler heads, and it is estimated that perhaps 25,000,000 have been installed by all sprinkler companies in this country. This represents an investment of nearly $75,000,000.

ALARM SERVICE

Fire protection is never considered complete without some form of alarm service. This service, in a general way, aims to prevent a fire from gaining great headway before being discovered. The common forms of alarm service are:

1. Watchman service.
2. Automatic alarm or thermostat systems.
3. Alarm valves on sprinkler systems.

Watchmen's Service.—There are watchmen and watchmen, one of the commonest type being the old employee who has passed his usefulness, as well as his youth, and is given the job of watchman because it is easy, and he is not good for much else. Another common type is the foreigner, whose chief recommendation is the low price at which he can be hired. There are, of course, many efficient watchmen who do their work well, but in no case can a watchman be depended upon unless he makes a record of his rounds. These rounds should be at least once an hour, as called for by the Insurance Requirements. The temptation to take a nap when the rest of the world is sleeping is too great for the average man when no checking system is employed.

The first forms of watchman's clocks were portable affairs containing dials which revolved with the hour hand. Keys were located at different points, and at each station the key was inserted in the clock and turned, thus embossing or puncturing the dial. Each morning the dial was removed and a new one inserted.

These keys were easily duplicated, and many a watchman has remained comfortably seated in the warm engine room, making his records without moving from his chair. In some cases the keys were removed from their stations and carried to the watchman's headquarters for safe keeping during the night. Others have gone so far as to unlock the clock and make an entire night's record at once, thus leaving the whole night free for an uninterrupted nap.

The next development was the electric clock, which was located permanently in the office or other suitable place. Wires were run from

here to each station and connected with a battery, so that when the button was pressed at the station an electric circuit was made and a dial punctured on the clock. This led to some of the brighter watchmen studying electricity and finding out how, by short circuiting the wires, the same result could be obtained without traveling to the distant stations.

Then came the Magneto systems, where a small magneto was located at each station and the handle at that point had to be turned in order to generate the current to puncture the dial. This effectually prevented "beating" the clock by the watchman, but still left an opportunity for improvement; for if a watchman was taken sick early in the evening, or perhaps dropped dead, nothing was known about it by his employers until the next morning. Meanwhile his duties as a watchman were not being performed. This led to the central station watchman's service, which has been used for several years. With this system there is no local clock, but the wires are run to a central station, such as that used for sprinkler supervision, and recorded on a tape machine similar to that used to record telegraphic messages. There is some one on duty at all times, and if the signals do not come in on time (a certain leeway always being allowed) a man is sent from the central station to investigate. This system is usually combined with a fire alarm system, so that by breaking the glass and pulling a hook a fire alarm can be sent in from each watchman's station.

Thermostat Alarm.—Automatic thermostats have been in use since about 1870. Various principles have been employed for this purpose. An ordinary thermometer with a platinum wire fused into the glass at where the mercury column would make contact with it when the temperature became excessive was one of the first, and this principle is still used. The device is, however, expensive and bulky, and has never been popular.

The first Watkins thermostat contained two small strips of dissimilar metals, such as brass and iron soldered together. When heated, these metals expanded unequally, thus causing the strip to bend. When sufficiently heated, the strip came in contact with a platinum point and made an electric circuit. This same principle has been used in all the various types of Watkins thermostats, from 1873 down to the present time.

The first type of thermostat made by the American Fire Alarm Company was patented in 1884, and consisted of a U-tube containing mercury, with the short end open. When heated, the mercury overflowed the tube and made electrical contact in a cup below. This was

bulky, fragile, difficult to adjust accurately, and liable to failure, owing to oxidation of the mercury. In 1885 it was superseded by the ether tube thermostat, which was used in various forms up to 1900. In this a curved bourdon spring is used, which is filled with ether and tightly sealed. When heated, the ether expands and causes the tube to straighten out and thus make electric contact.

Other old types contained coiled springs, expansive wax, etc.

About 1898 the solder release principle came into prominence, although it had been used much earlier in the "United States" and in other devices.

The objection to the earlier solder release types was that they were not sensitive enough, and when installed in the same plant with sprinklers the latter might operate first and cool the air so that no thermostatic alarm would be given.

Later types were made more sensitive by making the soldered joint small and insulating it from the rest of the device. As before stated, the lowest melting point for a permanent solder is about 160°, so that the same kind of solder had to be used as for sprinklers.

The only approved devices in New England today are the Wall and Woodman, both solder release devices, and the Watkins, where two dissimilar metals expand unequally.

Thermostats are installed in a somewhat similar manner as sprinklers, being attached to the ceiling and located 10 feet or less apart. The wiring is on a duplex system, so that the current can come two ways and one break will not cripple the system.

The Underwriters require a daily test of the system with records, but this testing device, together with the transmitting devices, is rather too complicated to explain at length here.

In cities the alarm is usually given at a central station, but in smaller towns and in the country it may be received at fire department houses, or at bells located in dwellings. An annunciator showing from which floor the alarm is received is attached to the outside of the building, except in central station equipments where the floor number is transmitted after the alarm. With central station system, a closed circuit is generally used.

FIRE DOORS, SHUTTERS, ETC.

Another important department of fire protection engineering covers the protection of buildings against a fire from outside. Up to the present, nothing has been discovered in the way of an economical building material

which is superior to brick as a fire retardent. A parapet brick wall, without openings, is, therefore, ideal for this purpose. Unfortunately, windows are often necessary, and the problem then becomes one of finding a suitable material for covering these windows.

Iron shutters about ¼ inch thick were the first to be used extensively. It was found that these warped in a bad fire, and they were finally replaced, to a large extent, by wood shutters, tin covered. These have been improved in regard to the joining of the tin, the kind of hardware used, etc., but the same general principle is used today.

This principle is, that if wood is covered so that the air cannot reach it, no combustion will take place. The reason for using wood is that it is cheap, easily worked, and of the required stiffness. The shutter is made of two thicknesses of ⅞ inch boards laid at right angles, then covered with double lock-jointed tin put on so that each joint is locked and no nail holes are exposed. When heated, the wood gradually carbonizes, but so long as the tin remains in place, it cannot burn. Such a shutter will stand a temperature of 1,500 to 1,700° F. for an hour and still hold its shape.

Fire doors are built on the same principle, except that three thicknesses of wood are now required. These are of larger area than shutters, and two thicknesses were found insufficient to withstand a severe fire.

Numerous other doors and shutters have been put on the market of late years, built of asbestos board, paneled steel, cement-filled metal, etc., but none that are of standard fire-resisting qualities are cheap enough to come into general use.

Wired Glass

Wired glass windows in hollow metal frames have been used for the past six or eight years, and are replacing shutters to some extent. They have the advantage of being more easily closed, and, furthermore, they are more apt to be closed when needed. They are as good a fire retardent as shutters, except for the fact that they transmit heat readily.

Combustible material located within a foot of the glass can readily be set on fire by radiated heat, but if there is no combustible material near by, these windows form a very satisfactory fire stop.

Wired glass is ¼ to ⅜ inch thick and contains a coarse wire netting embedded in the centre. It can be heated almost to red heat and have water thrown upon it without breaking apart. The glass is cracked into thousands of pieces, but the wire netting holds it in place.

There are detailed rules for the construction of the sash which we have not time to consider.

Open Sprinklers

Another form of protection for windows is open sprinklers (Fig. 13). These are specially designed sprinkler heads, with outlet open at all times, arranged to be placed at the top of a window or under a cornice. They are also made for the peaks of shingle roofs. The piping is arranged in a somewhat similar manner as with automatic sprinklers, but the main valve is kept closed and only opened in case of fire. While they are of considerable value, still the protection they afford cannot be considered the equivalent of standard shutters or wired glass windows.

Fig. 13.—Grinnell Open Sprinkler

Designed to be placed at top of window or under cornice and form a water curtain on the exterior of a building.

HOSE, HYDRANTS, ETC.

Considerable might be said in regard to hose, hydrants, play pipes, and fire department apparatus, but time does not permit.

Leather hose was used up to thirty or forty years ago, when linen and rubber replaced it. The standard today is cotton, rubber-lined, and the specifications call for high grade rubber of a considerable thickness. The modern play pipe for use in private plants is of brass, 30 inches long, with tapered outlet 1⅛ inches in diameter. The whole is wound with painted cord and fitted with swivel handles. The monitor nozzle is used considerably on the roofs of high buildings, in large, high-studded sheds where sprinklers are not entirely feasible, and in other places.

The modern steam fire engines are familiar to every one, and their size and capacity are constantly increasing.

Chemical extinguishers are also used extensively by fire departments, and the smaller types give excellent protection in factories and dwelling houses. They, too, have been greatly improved since they were first used, thirty or forty years ago.

In closing, I would like to make a few practical suggestions for lessening the annual fire waste and the fearful loss of life which it entails. Such horrors as the Iroquois Theatre fire, the steamship *Slocum* disaster, and the recent school fire in Collinwood can be prevented, and it is largely a matter of arousing public sentiment in order to have the necessary remedies applied.

First, prevention of fires. This is a matter that lies almost entirely in the hands of individuals. No fire department, no sprinkler system, no device of any kind can prevent a fire from starting. Fires are caused largely by carelessness. If every one should see that no rubbish is allowed to accumulate on his premises, that all oily waste is burned before it ignites spontaneously, that stoves and furnaces are properly arranged, that only safety matches are used, and that all other cautions that common sense dictates are strictly adhered to, we should at least have made a good start.

Second, the prevention of the spread of fire. This can be done by improved construction, by improved private protection, and by maintaining the most efficient fire departments. If every owner of a fire trap should equip it with automatic sprinklers, and if every owner of a well-constructed but exposed building should protect all window and other outside openings in a standard manner, then conflagrations would be practically eliminated. It is perhaps too much to hope that such improvements can be made by the free will of the owners, but it is perfectly practical to pass laws which will require it. Theatres can be made safe by equipping the stage section with automatic sprinklers, installing approved automatic vents over the stage, and making a proper fire cut-off between the stage and auditorium by means of fire doors, asbestos curtain, and water curtain. Schoolhouses can be made safe by building them first of fireproof construction, or by placing automatic sprinklers in all sections where a fire is liable to start, and then putting stairways in cut-off towers, etc. It is only a matter of arousing public sentiment, and these improvements will be forced upon those who are responsible for these conditions.

The cost of these changes is not prohibitive; in fact, in most cases it is entirely offset by the reduction in insurance rate.

Refuse to patronize unsafe theatres, refuse to send your children to schools that are fire traps, refuse to travel in crowded excursion boats which are entirely without adequate fire protection, and you will be doing your part toward preventing the recurrence of these disasters.

CONTRIBUTIONS FROM THE
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
No. 31

AN IMPROVED APPARATUS FOR THE MEASUREMENT OF TRANSFERENCE NUMBERS IN SOLUTIONS OF THE HALOGEN ACIDS AND THEIR SALTS

BY EDWARD W. WASHBURN

I. INTRODUCTION

THE apparatus and method described in this communication were devised for the purpose of studying the true transference numbers and relative ionic hydrations in solutions of the alkali chlorides, an investigation which required the application of the Hittorf method with the highest possible accuracy. Since the apparatus is of general applicability in transference experiments by this method, and as it embodies several improvements over previous forms, it has seemed desirable to describe it at this time, leaving for a future communication the results of its application to the study of the problem of hydration in solution.

The conditions which must be fulfilled in order to attain the highest degree of accuracy in a transference measurement by the Hittorf method may all be summed up in the following statements:

1. The passage of electricity from electrode to solution or from solution to electrode must take place by one path only, that is, side reactions and partial secondary reactions must be excluded.

2. The amount of electrolyte transferred and the concentration changes resulting at the electrodes should both be as large as possible.

3. The amount of electricity passed through the solution must be accurately known.

The first condition depends upon the nature of the electrodes, while the second condition, once the electrodes are determined, is dependent chiefly upon the form of the apparatus used. We shall proceed to the consideration of each condition separately.

II. The Electrodes

If a solution of an alkali chloride be electrolyzed between platinum electrodes, hydrogen and hydroxyl ions are formed at anode and cathode, respectively. These rapidly moving ions soon migrate away from the electrodes and mix with the electrolyte in the middle portion of the solution. To avoid the formation of hydrogen ion, Hittorf[1] used a cadmium anode, placing it at the bottom of his apparatus. The slowly moving cadmium ions which formed around this electrode effectually prevented any stirring. This use of a soluble anode (usually cadmium or zinc) to avoid the formation of hydrogen ion was followed also by Hopfgartner,[2] Bein,[3] and Jahn[4] in their investigations. According to Bein, the use of these soluble anodes is complicated by side reactions resulting in the formation of basic salts. This statement, however, is contradicted by Jahn, who could find no evidence of any such action.

To prevent the formation of alkali at the cathode, Hopfgartner and Jahn used a mercury electrode covered with a layer of a strong solution of the salt of some metal which amalgamated readily with mercury, usually zinc or copper. These devices effectually prevent the formation of the rapidly moving hydrogen and hydroxyl ions and the evolution of gas at the electrode. (This latter effect is to be avoided, owing to its tendency to produce stirring and to carry away mechanically a portion of the solution in the form of a fine spray.) They have the disadvantage, however, of introducing foreign ions into the solution, thus preventing a large transport of electrolyte and complicating the analyses. Noyes,[5] in his investigation of the transference numbers of the alkaline-earth metals, modified the method by making both electrodes of platinum and by adding during the electrolysis, at the anode and cathode, respectively, measured quantities of alkali and of acid, so as to keep the solution at a uniform concentration and to prevent the formation and migration away from the electrodes of hydrogen or hydroxyl ion. By this means he was able to obviate the above mentioned difficulties and to obtain a much larger transport of electrolyte than any of the previous investigators.

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[1] Hittorf, Pogg. Ann., 106 (1859).

[2] Hopfgartner, Z. physik. Chem., 25, 115 (1898).

[3] Bein, Z. physik. Chem., 27, 1 (1898).

[4] Jahn, Z. physik. Chem., 37, 675 (1901).

[5] Noyes, J. Am. Chem. Soc., 23, 148 (1901).

Obviously the ideal electrodes to use in a transference measurement would be composed of the metal whose salt was under investigation. The process then would consist simply in the formation of the metal ion at the anode and its discharge at the cathode, accompanied by the transference of T equivalents of the salt from one electrode to the other. While in the case of the alkali halides we cannot use the reversible metal electrodes, we can attain the same result by using reversible electrodes composed of the corresponding insoluble halide salt of some other metal, such as silver. Thus, if one equivalent of electricity be passed through a sodium chloride solution between silver chloride electrodes, or more strictly speaking between a silver anode and silver chloride cathode, the process which takes place consists essentially in the formation of chloride-ion at the cathode and its discharge at the anode where insoluble silver chloride is formed. At the same time T equivalents of electrolyte are transferred from anode to cathode, T being the transference number of the cation. By means of this simple arrangement it is possible to carry on the electrolysis without the formation of any acid or alkali, or the evolution of any gas, or the introduction of any foreign substance into the solution. The present investigation has dealt only with the preparation and use of silver chloride electrodes. A few qualitative experiments with silver iodide and bromide electrodes, however, indicate that when prepared in an analogous manner they also will give good results.

Preparation of the Silver Anode.—The use of a silver anode[1] for transference work with solutions of chlorides was introduced by Noyes and Sammet[2] in their transference measurements on hydrochloric acid. If a solution of a chloride be electrolyzed, using a silver rod as the anode, the following series of phenomena take place. The bottom of the rod is first attacked and a coating of dark gray silver chloride is formed, which extends slowly upward until the rod is entirely covered. The layer gradually increases in thickness, and the potential between electrode and solution rises until oxygen begins to be evolved and the solution becomes acid in the vicinity of the electrode. At the same time the layer of chloride near the bottom of the rod begins to turn white, and finally, as the electrolyte in the vicinity of the electrode becomes

[1] In McBain's compilation (see page 177 of this paper) incorrectly given as platinum anode.

[2] Noyes and Sammet, J. Am. Chem. Soc., 24, 947 (1902).

exhausted, a white cloud of colloidal silver chloride is given off from the electrode and migrates downward with the current.

If the current density is increased, gaseous chlorine is also evolved at the electrode. Noyes and Sammet found that with a current density of not more than 4.5 milliamperes per square centimeter no chlorine was evolved, but the formation and migration of the cloud of silver chloride from the electrode was always obtained, as was also the liberation of oxygen and the formation of an equivalent amount of acid in the solution. In the analysis of their anode portion they were therefore obliged to dissolve the silver chloride from the anode by means of ammonia, and determine it along with the total chloride in the anode portion. This formation of acid can, however, be entirely prevented by using an electrode with a sufficiently large surface and taking precautions to prevent the exhaustion of the electrolyte in its immediate vicinity. At the same time a closely adherent layer of dark gray silver chloride is obtained, and the formation of the white colloid in the solution is entirely prevented. Two types of anodes were used in the present investigation. Type A, made from silver wire, is best adapted for use with dilute solutions, say from 0.2 molal down. For more concentrated solutions, a much larger surface of electrode must be available, and type B was devised to meet this requirement.

Preparation of Type A Anode.—This anode is made of No. 21 B. & S. gauge, pure silver wire (diameter 0.7 mm.), which is wound into a loose spindle about 3 cm. long and 2.2 cm. in diameter. In order to secure the necessary distance between the successive layers of the coil, each layer is separated from the preceding one by a few sheets of gun cotton, which is burned out after the coil is completed. The gun cotton is prepared by the nitration of an ashless filter paper in a mixture of three parts of concentrated sulphuric and one part of fuming nitric acid for forty-eight hours, followed by a thorough washing. When properly prepared, these gun cotton layers burn out readily, leaving an electrode with a large surface easily permeable by the solution in all its parts. After burning out the gun cotton, the electrode is plunged into warm dilute nitric acid until it is attacked violently, washed with boiling distilled water and then with alcohol, the excess of which is finally removed by ignition. This treatment removes the grease and dirt and imparts a matte surface to the wire, in which condition it is more readily attacked by the chlorine.

Preparation of Type B Anode.—A silver wire of suitable length is

wound into a flat spiral, the ends being brought up vertically through the centre of the spiral and twisted together to form the lead wire. The spiral is placed in the bottom of a filter paper tube, as shown in the

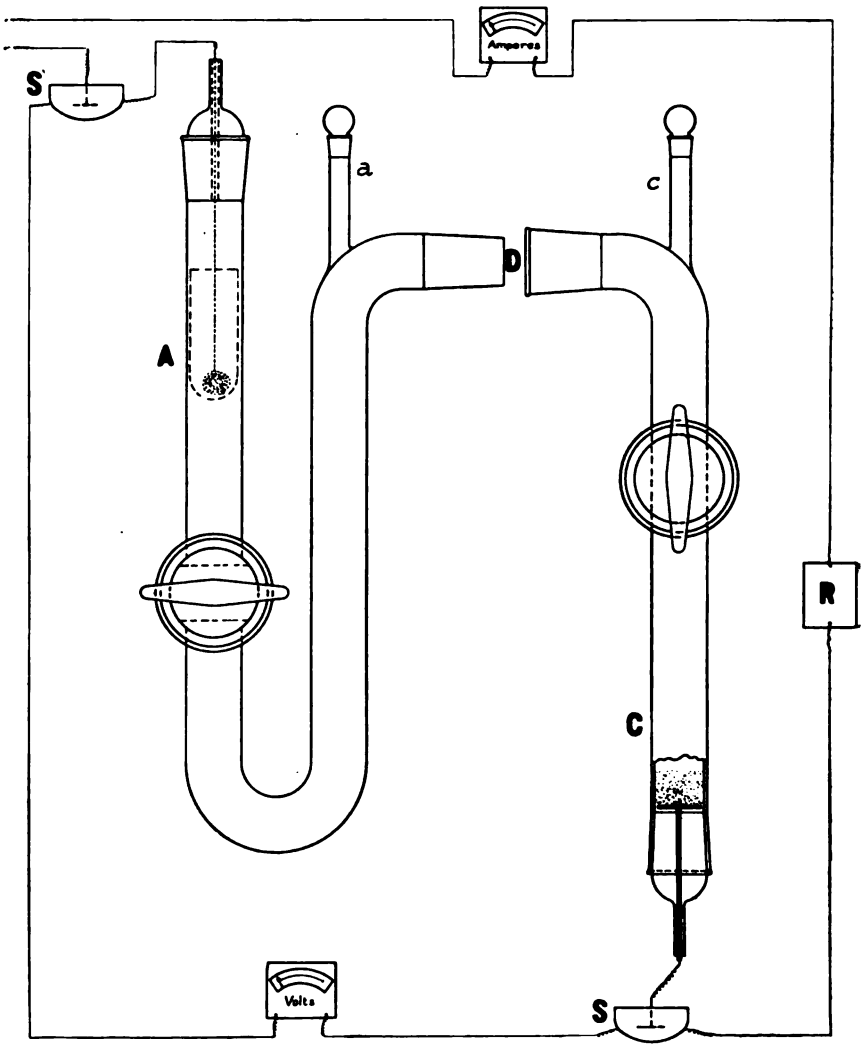

FIG. 1.—DIAGRAM OF APPARATUS AND CONNECTIONS

diagram (Fig. 1). The tubes used for this purpose are the familiar Soxhlet extraction cartridges, which can be purchased in several sizes. The size to be used depends upon the dimensions of the apparatus and

the amount of electricity to be sent through it. Those used in the present investigation were 6 cm. long and 1.9 cm. in diameter.

After the wire is in place, the cartridge is filled with "electrolytic crystals" of pure silver, which are packed tightly around the lēad wire. These crystals are prepared by the electrolysis of a silver nitrate solution with a silver anode and platinum cathode. The clusters of crystals so obtained are broken up somewhat and are then washed with hot water and finally with methyl alcohol, which is removed by ignition. The result is a mass of bright crystals of pure silver, which when packed in the cartridge as described give a silver electrode of maximum surface in the minimum volume. When the electrode is prepared, the filter paper cartridge is punctured with numerous needle holes to ensure ready penetration of the solution throughout the mass of silver. This form of electrode has been found to be eminently satisfactory. All of the silver surface is available as electrode, the crystals being changed to silver chloride without losing their form or porosity. Moreover, the electrode is easily broken up and mixed with the anode portion when the electrolysis is completed. An electrode of the above dimensions will carry a current of 0.1 ampere for sixteen hours without the formation of the slightest trace of acid or of colloidal silver chloride in the solution.

Preparation of the Silver Chloride Cathode.—This electrode consists essentially of a silver disk covered with the necessary amount of granular silver chloride. The disk is of such a diameter as to just slip into the apparatus tube. A silver rod welded into its centre passes out through the stopper of the apparatus, where it is joined to the lēad wire, as shown in the diagram. The disk is first cleaned by plunging it into warm nitric acid and is then suspended in a normal sodium chloride solution in a U-tube. Using it as an anode, a current of 0.025 ampere is passed through the solution until gas is evolved freely at the anode. The electrode is then removed, washed thoroughly with hot water and dried. The rod is then drawn through the opening in the stopper of the apparatus and cemented firmly in place, after which the stopper is inserted in the apparatus and a suspension of silver chloride is poured in until a column of the desired thickness is formed upon the electrode.

The silver chloride for this purpose is prepared by precipitating a hot solution of silver nitrate with an excess of an alkali chloride solution and washing thoroughly with boiling water. The precipitate is then washed by decantation with the stock solution of the alkali chloride

under investigation, until the liquid in contact with it has the same composition as the stock solution. This mixture is then poured upon the cathode by means of a thistle tube reaching nearly to the bottom of the cathode half of the apparatus. After the silver chloride has settled, the supernatant liquid is pipetted off, and after filling the apparatus the electrode is ready for use. During the passage of the current the silver chloride is reduced to gray metallic silver. It is only necessary to keep the current density low enough so that the rate of solution of the silver chloride is sufficiently rapid to supply the necessary amount of silver ion to carry the current from solution to electrode. An electrode 2.3 cm. in diameter will carry 0.5 ampere without the evolution of hydrogen or the formation of the slightest trace of alkali. It has been found that the physical condition of the silver chloride plays an important part in this action. If it is prepared by precipitation in the cold, it fails to act as a depolarizer. Boiling the precipitate seems to affect its physical condition so as to render it more soluble or more easily reduced. It should, of course, be protected from the action of white light.

III. The Apparatus

It is very desirable that the apparatus for transference experiments be as simple in form as is consistent with its main requirement, which is to secure the maximum transport of electrolyte and the maximum concentration change at the electrodes. The chief disturbing element is the mixing of the solution around the electrode with the rest of the solution. This may be caused by diffusion, by convection due to heat developed by the current, or by currents set up when the different portions of the solution are separated from one another at the end of the experiment.

The form of apparatus[1] finally adopted is designed to reduce these effects to a minimum. It is a modified form of the apparatus used by A. A. Noyes in his investigation of the transference numbers of the alkaline-earth metals.[2] It is shown in Figure 1. The anode tube, *A*,

[1] The apparatus designed for this investigation was constructed by Mr. Otto Pressler, of Leipzig, under the direction of Dr. W. Böttger, who was a Research Associate in this laboratory at the time this investigation was begun (1904–05), and who kindly offered to superintend the construction of the apparatus for me upon his return to Leipzig the following year. The construction of the apparatus offered considerable difficulty at first, owing chiefly to the size of the stopcocks, and I gladly take this opportunity to express my indebtedness to Dr. Böttger, to whose kindness and friendly interest is largely due the final construction of a satisfactory apparatus.

[2] Noyes, J. Am. Chem. Soc., 24, 946 (1902).

is a U-tube having the top of its shorter arm bent at right angles and fitted by means of a ground glass joint, *D*, into the corresponding portion of the cathode tube, *C*. The short tubes, *a* and *c*, are provided with glass stoppers and serve to admit the stem of a pipette for the removal of the solution. The top of the anode tube *A* is fitted with a ground glass stopper carrying a small tube sealed through its centre for the admission of the lead wire to the anode. The bottom of the cathode tube *C* is provided with a similar stopper. As soon as the cathode disk has been prepared as directed above, its lead wire is sealed into the small tube with Khotinsky cement and the stopper is then sealed in place with the same cement.

The two large stopcocks serve to cut off the two electrode portions when the electrolysis is finished. The *whole* apparatus is of uniform bore (2.3 cm. diameter) throughout, including the cross tubes of the stopcocks. This is essential in order to prevent local heating and consequent stirring during the passage of the current. The apparatus is kept in a water thermostat at constant temperature during the passage of the current. The keys of the two stopcocks are hollow, the rear face of each being cut off so that the water of the thermostat can circulate about the cross tube. Apparatus and support are shown in the photograph, Fig. 2.

IV. Procedure of a Transference Experiment

Setting up the Apparatus.—The apparatus is cleaned thoroughly with warm chromic acid solution, and after washing with water and drying with pure alcohol the two tubes are placed in their supports, as shown in the photograph. Each stopcock is slightly greased with vaseline, the surface immediately opposite the cross tube being, however, left free from vaseline, so that on closing the cock the lubricant will not come in contact with the solution in the apparatus. After the insertion and alignment of the stopcocks, a thin layer of melted paraffin is applied by means of a camel's-hair brush to the joint between the key and the sheath, both front and rear. This paraffin seal entirely prevents all connection between the solution in the apparatus and the water of the thermostat, and at the same time allows the cock to be turned easily.

After the insertion of the electrodes the two halves of the apparatus are joined at the ground glass joint, which is also lubricated with vase-

FIG. 2.—PHOTOGRAPH OF APPARATUS AND STAND

line[1] and protected with the paraffin seal in the same manner as the stopcocks. The lead wires from the electrodes are protected from the water of the thermostat by rubber tubes which are brought out through rubber bushings in the side of the thermostat and the wires connected to binding posts. As a further precaution a piece of rubber band tubing is drawn over the bottom of the cathode tube as far as the stopper, and is then brought up above the surface of the water.

After filling the apparatus with the stock solution, the anode is moved up and down a few times to remove air bubbles, and is then fixed so as to occupy a position about three centimeters above the stopcock. This arrangement leaves considerable solution above the electrode, which stirs slowly during the run and prevents the exhaustion of the electrolyte in the immediate vicinity of the electrode. The three glass stoppers at the top of the apparatus are sealed with the paraffin seal, and the whole apparatus is placed in the thermostat to such a depth that the water and the solution in the tube are at the same level.

The connections are made as shown in the diagram. Two silver coulometers, *S*, one connected to the anode and the other to the cathode, serve to detect any leakage during the passage of the current. After the solution has come to the temperature of the thermostat, the circuit is closed and the rheostat, *R*, adjusted to the proper current strength. The voltmeter which is connected in shunt just outside the coulometers serves to indicate the progress of the electrolysis. During the first hour or two the potential across the apparatus gradually falls to a value which remains constant until near the end of the run, when it begins to rise gradually. This increase begins when the whole surface of the anode is covered with the chloride layer. When the potential has risen one volt, the circuit must be broken or oxygen will be evolved at the anode.

Removal of the Solution.—As soon as the circuit is broken the two stopcocks are closed, and by introducing a pipette into the apparatus through the small tube on the cathode side the solution is drawn out of the horizontal portion of the tube and down to the cathode stopcock. This portion, which will be called the cathode middle portion (M_c), is transferred to a 150 c.c. glass-stoppered, tared, Erlenmeyer flask. In a similar manner two other portions are removed; the middle portion (M), which extends down to the bend in the anode tube, and the anode middle portion (M_a), which comprises the rest of the solution around to the anode stopcock.

[1] The vaseline used for lubrication should be freed from all soluble matter by repeated extraction with boiling water.

After the removal of these portions the apparatus is taken from the thermostat, dried on the outside, the rubber tubes removed, and the cathode lead wire disconnected. The two halves of the apparatus are disconnected at the ground glass joint and paraffined rubber stoppers are inserted in each. After first opening the stopcock, the contents of the cathode tube are mixed thoroughly, and then after sealing all joints with paraffin it is set aside to allow the silver and silver chloride to settle out. The anode stopcock is opened and the anode lowered until it can be caught between the stopcock and the wall of the tube. In this manner it can be broken up and mixed with the solution. After thorough mixing, this half of the apparatus is also sealed with paraffin and set aside to allow the silver chloride and filter paper shreds to settle.

Each half of the apparatus is cleaned and dried on the outside and weighed to the nearest centigram. The bulk of the clear solution is removed with a pipette and transferred to a small, glass-stoppered Erlenmeyer flask. The residue from the electrode is washed out into a beaker, and after drying the empty apparatus with alcohol and ether it is weighed. The electrode residue of silver and silver chloride is collected on a filter, washed with alcohol and ether, dried and weighed. The necessary data for calculating the total weight of the electrode portion are thus obtained.

V. The Coulometers

The silver coulometers used in this investigation were of the ordinary type, the cathode consisting of a platinum disk and the anode of a silver disk covered with a close filter paper. Guthe[1] has recently shown that the results obtained with this type do not differ by more than 0.05 per cent. from those obtained with the more accurate Richards type, a degree of accuracy which is amply sufficient for transference work. The silver nitrate solution for the coulometers was freshly prepared for each experiment.

VI. Experimental Results

To illustrate the character of the results which can be obtained with this apparatus, the data of two runs with 1.2 molal KCl solution are given in the accompanying table. The temperature of the thermo-

[1] Guthe, Bull. Bureau Stand's, 1, 28 (1904).

stat was maintained at 25° and the current strength at 0.1 ampere for twelve to fourteen hours, the drop of potential through the apparatus being 18 volts.

TABLE

	Run I.	Run II.
Ag deposited in coulometer (A)	5.0866	5.3685
Weight of electrode portion (A)	99.83	103.21
Percentage of KCl in portion (A)	6.790	6.510
Percentage of KCl in portion (M_a)	8.346	8.105
Percentage of KCl in portion (M)	8.348	8.108
Percentage of KCl in portion (M_c)	8.349	8.108
Percentage of KCl in portion (C)	10.168	10.03
Weight of electrode portion (C)	85.72	85.28
Ag deposited in coulometer (C)	5.0855	5.3681
Equivalents of electricity passed through	0.04713	0.04974
Grams of KCl transferred (A)	1.696	1.794
Grams of KCl transferred (C)	1.703	1.784
Therefore transference number of anion (A)	0.518	0.517
Therefore transference number of anion (C)	0.516	0.519

These results illustrate the exactness with which the two electrode portions can be cut off from the adjoining middle portions without any mixing. In most cases the changes in these middle portions are so small that no correction need be applied for them. It is essential that more than one middle portion be obtained and analyzed in transference work. If only a single middle portion be taken, it may be found on analysis to be practically unchanged, even though mixing has taken place with *both* electrode portions, since these two effects would tend to counterbalance each other. With three middle portions, however, all uncertainty on this point is removed.

The calculation of the transference numbers given in the above table was made in the usual manner. That is, the mass of solvent (m_s) in the electrode portion is multiplied by the ratio of electrolyte to solvent in the original solution, thus giving the mass of the electrolyte in m_s

grams of solvent before the electrolysis, whence by subtracting the mass of electrolyte in the electrode portion the amount of electrolyte transferred is obtained. The number of equivalents of electrolyte transferred, divided by the number of equivalents of electricity passed through the solution, gives the *ordinary transference number* of the anion, T_s^a. In this method of calculation the assumption must be made that the solvent is absolutely stationary, that is, that no transfer of solvent takes place from one electrode to the other. If such a transfer of solvent takes place, which would be the case if the ions were hydrated and carried water with them as they moved through the solution, the calculation of the transference number by the above method is not justified and will not give the *true transference number*, T_t. In fact, the number so obtained does not represent any physical quantity. Only in dilute solutions, where the amount of solvent transferred becomes negligible in comparison with the total solvent present, will the ordinary transference number T_s approach the true one, T_t. The measurement of the relative ionic hydrations and *true* transference numbers by means of this apparatus will be described in a future communication.

VII. Modification of the Apparatus for Use with Dilute Solutions

The procedure as described above is applicable only to comparatively concentrated solutions, say from 0.2 molal up. For more dilute solutions the apparatus is modified slightly in order to effect the necessary amount of transport of electrolyte and to provide a larger amount of solution for analysis. This is effected at the anode by increasing the length of the anode tube above the stopcock without, however, altering the position of the electrode, which in this case is type A. The increased amount of electrolyte above the anode stirs during the run, thus supplying the necessary amount of chloride ion for carrying the current to this electrode and allowing a corresponding greater transport to be obtained. It is better to obtain this increase in electrolyte by increasing the depth of solution above the electrode rather than by using an apparatus of larger cross section, since as the diameter of the tube increases it becomes more and more difficult to maintain a constant temperature throughout the tube and avoid the convection currents due to heating. At the cathode the increased volume is secured by an expansion of the tube for a short distance above the electrode. The same apparatus can

be employed for both concentrated and dilute solutions by having the two additional tubes ground to fit the same socket as the stoppers, so that they can be inserted when desired.

As an additional precaution against stirring, the use of diaphragms will be found advantageous for the more dilute solutions. These diaphragms, which are made of a medium-mesh silk bolting cloth, are conveniently inserted in the cross tubes of the stopcocks. The cloth is drawn over a thin vulcanite ring, which is then pressed into the cross tube of the stopcock, which it just fits. Hittorf[1] has shown that diaphragms of this character do not produce cataphoresis.

NOTE. — An excellent and exhaustive compilation and criticism of all transference work up to the end of 1905 will be found in a paper by J. W. McBain. [Proc. Wash. Acad. Sci., 9, 1 (1907)]. [Univ. Toronto Pub. No. 67.]

Boston, June 1, 1908.

[1] Hittorf, Z. Phys. Chem., 39, 617 (1902).

DEMONSTRATION APPARATUS FOR ILLUSTRATING COMMUTATION[1]

By HARRISON W. SMITH

It is well known that sparkless commutation in direct-current machines occurs when the current in any armature coil, at the end of the period during which it is short-circuited by a brush, is equal in magnitude but opposite in direction to the current which was flowing in it at the beginning of short-circuit. In order that this may take place, the current which is flowing in the coil at the beginning of short-circuit must fall to zero, and a new current must be established in the reverse direction and equal, at the instant short-circuit ceases, to the initial current. The chief factor in accomplishing this reversal of current is the commutating E.M.F., which may be obtained by moving the brushes so that the coils are short-circuited in the proper "commutating field," or by furnishing the commutating field through the use of special commutating poles. A second important factor is the contact resistance of the brush when carbon brushes are employed.

For the purpose of illustrating these features of commutation two pieces of apparatus have been devised for use at the Massachusetts Institute of Technology. One shows how commutation with a low-resistance metallic brush is affected by the magnitude of the reversing E.M.F., by the self-inductance of the coil, by the magnitude of the current to be reversed, and by the time available for commutation. Another piece of apparatus shows how commutation is assisted by a brush of high contact resistance independent of all other factors.

Figure 1 is from a photograph of the apparatus for illustrating the features associated with commutating E.M.F., and Figure 2 is a diagram of its connections. Brushes B and B', built up of $\frac{1}{4}$-inch strips of brass, rest on a two-part commutator and convey a current from constant potential 230-volt mains. This current, which is to be reversed by the commutator C, may be varied in magnitude by the lamps L, L, L, L.

[1] Reprinted from The Electrician, January 17, 1908.

From the commutator *C* the current is taken by slip-rings through a coil, *H*, wound on a laminated iron core with a variable air-gap for the purpose of giving variable inductance, this coil obviously representing one of the coils on an armature as far as the reversal of current through it is concerned. In series with this coil is a double-throw switch, *S*, and the circuit is complete through the coil *H* alone when the switch is thrown to the left. Commutator *C* can be rotated by a small motor at speeds varying from 70 to 300 revolutions per minute. Brushes *B* and *B'*, placed diametrically opposite, are each ⅜ inch in width, while the gap

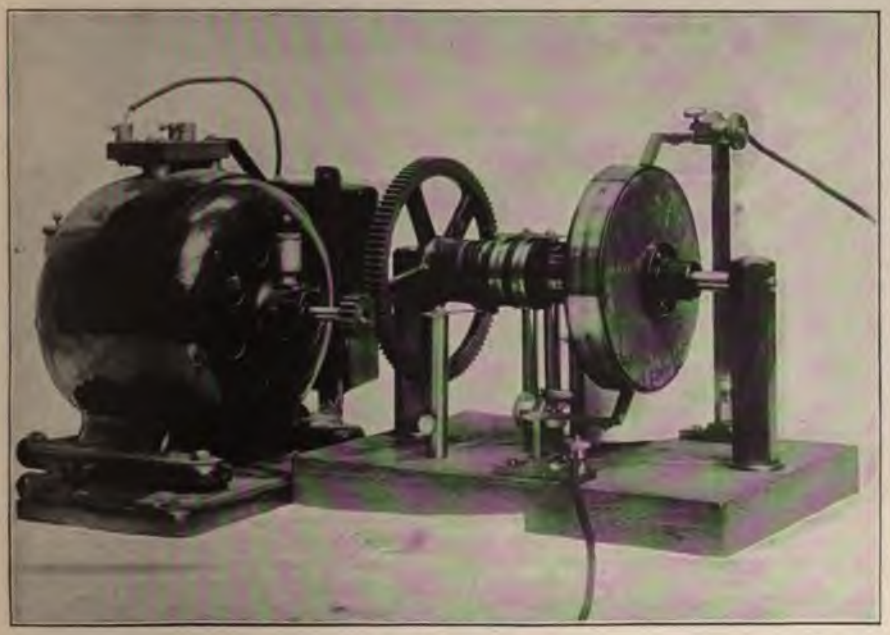

FIG. 1

between the segments of the commutator is ⅛ inch. It is evident, then, that the segments of the commutator, and consequently coil *H*, will be short-circuited by both brushes simultaneously, and that short-circuit will cease at very nearly the same instant at both brushes. In fact, of course, slight irregularities in the edge of the segments will cause either brush *B* or *B'* to maintain short-circuit longer than the other, and whatever spark occurs will be seen at one brush only. It is desirable, therefore, to advance the upper brush *B* enough to cause short-circuit of the segments to cease always at brush *B'* just before the contact of *B* with the receding

segment is broken. In this way the process of commutation begins when B' short-circuits the segments and ends when B opens the circuit between itself and the receding segment. The advantage of this arrangement consists merely in having the spark occur at the upper brush, where it is most easily visible.

If, now, the switch S is closed to the left and the commutator caused to rotate, a spark will appear at B, the length of the spark being proportional approximately to the time necessary to build up the current in coil H.

In order to introduce an E.M.F. into the coil H the switch S is thrown to the right, the circuit of the coil then including an additional commutator, C', and a storage battery so arranged as to give an E.M.F.

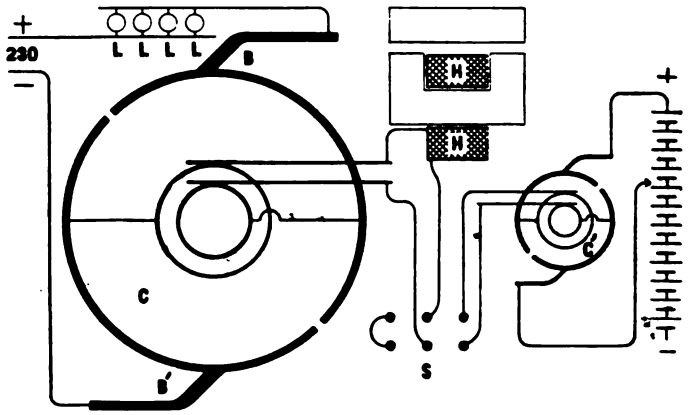

FIG. 2

variable from 2 to 24 volts. The commutator C' is placed on the same shaft with C, the two planes of commutation being normal to each other. As shown in Figure 2, the battery E.M.F. is evidently aiding the current in the coil, but after the commutator has rotated one quarter revolution it is evident that the battery E.M.F. will be opposing the flow of current through the coil. This connection of the battery with respect to coil H continues until after commutation has been effected, so that the battery E.M.F. will evidently assist in reversing the current in the coil as long as the segments of commutator C are short-circuited by brush B or B'. This battery, then, by the action of the commutator C', supplies an E.M.F. which acts precisely as the reversing E.M.F. in an ordinary armature.

The diameter of commutator C is 6 inches and of C' 2 inches. The coil H contains 300 turns of No. 12 Brown and Sharp gauge magnet wire wound on a laminated iron core 2.5 inches square.

A large number of experiments are at once suggested. Let the switch *S* be thrown to the left and a number of different brushes used successively at *B* varying in width from ⅜ inch to 1½ inches. Turn on lamps to give about 1.5 amperes from 230-volt mains. A spark will always occur, even with very low speeds, showing that no matter how wide the low-resistance brush be made, sparkless commutation cannot be obtained without a reversing E.M.F. Next, with the ⅜-inch brush at *B*, the commutator revolving about 70 revolutions per minute, the coil *H* adjusted for minimum inductance, and switch *S* thrown to the right, adjust the battery until no spark occurs. This will require about 6 volts. Either a larger or a smaller value of battery E.M.F. will cause sparks due to excessive or insufficient reversing E.M.F. Increase the current by turning on more lamps at *L*, and more battery E.M.F. must

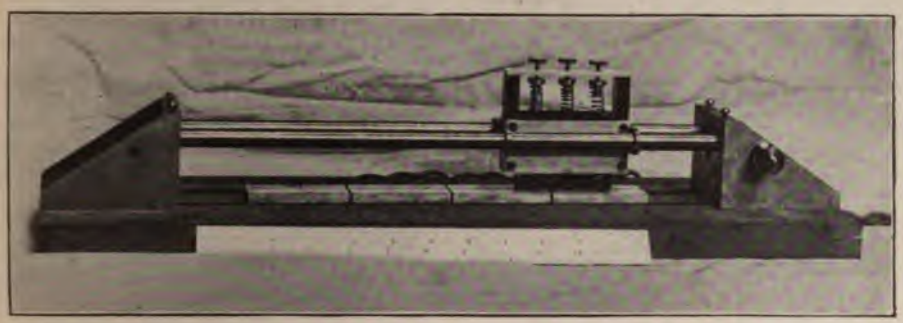

FIG. 3

be employed to prevent sparking. Next increase the inductance of *H*, which will require a larger reversing E.M.F., thus emphasizing the necessity of keeping down the inductance of armature coils. Again adjust the battery to give sparkless commutation, and substitute for the ⅜-inch brush the 1¼-inch brush without changing any other factors. A spark will now appear, due to excessive reversing E.M.F., and may be eliminated by reducing the reversing E.M.F., thus emphasizing the time element in commutation. Changing the speed of the commutator still further illustrates this feature. Let the speed of the commutator be increased, and sparks will appear which can be eliminated by reducing the inductance of *H*, by increasing the reversing E.M.F., or by using a wider brush.

In order to demonstrate the action of brush contact resistance in assisting commutation, the apparatus illustrated in Figure 3 is serviceable.

The electrical connections are shown in Figure 4, and this will at once be recognized as an adaptation of the method of discussion to be found in most treatises on the subject. Four brass plates, S_1, S_2, S_3, and S_4, representing four segments of a simple bipolar armature, are fastened to a slate base, and a carbon brush, B, can be drawn slowly across the segments, pressing firmly upon them.

Between the segments are placed three 5-ampere ammeters, having the zero point at the middle of the scale and representing three coils on the armature. The two paths through the armature are completed by two banks of lamps, L_1 and L_2, adjusted to take 5 amperes each from 115-volt constant potential mains. The currents from L_1 and L_2, after flowing into S_1 and S_4, respectively, unite in the brush B; and it is evi-

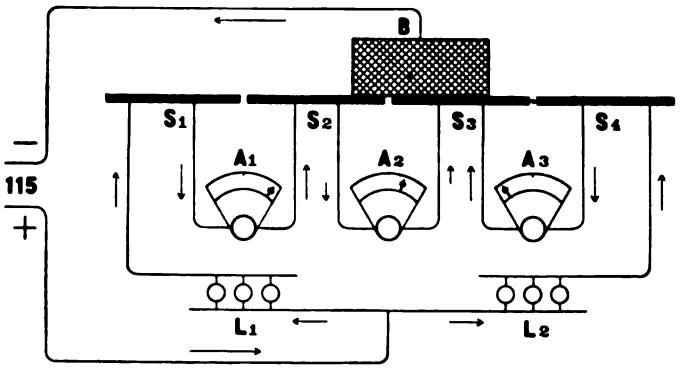

FIG. 4

dent that if B rested wholly on S_3 the current through A_1 and A_2 would flow from left to right, while the current through A_3 would flow in the opposite direction.

The diagram shows one-quarter of the brush resting on S_2 and three-quarters on S_3. If, then, the contact resistance of the brush is large compared with the resistance of the ammeter A_2, one-quarter of the current entering B, or 2.5 amperes, must flow from S_2; and since the current entering S_2 is 5 amperes, there must be 2.5 amperes flowing from S_2 into S_3. If it is considered that the brush is moving from right to left, it is evident that the current in A_2, which was 5 amperes when B rested wholly on S_3, has decreased to 2.5 amperes at the moment the brush is in the position shown, and that as the brush moves from the position where it rests wholly on S_3 to the position where it rests wholly

on S_2 the current in A_2 is gradually reversed. The arrows indicate in length the magnitude of the current in different portions of the circuit. It is evident that 1 ammeter would be sufficient, but the experiment is made more effective by drawing the brush across all four segments, starting at S_4, in order to show the successive reversal of current in adjacent coils. The brush is beveled so as to give a contact surface about ⅛ inch wide by 2½ inches long, in order to increase the contact resistance. The other dimensions are approximately indicated by a 1-foot scale resting beside the slate base in Figure 3.

SERVICE TEST ON THE STEAMSHIP GOVERNOR COBB[1]

(PARSON'S TURBINE)

By W. S. LELAND and H. A. EVERETT

The test on the steamship *Governor Cobb*, of the Eastern Steamship Company, was run by the Massachusetts Institute of Technology to provide thesis work for some of the graduates in the Department of Naval Architecture.

The test was run under service conditions on the regular trip of the *Cobb* from Boston to St. Johns, via Portland and Lubec. Observations began on passing Boston Light and were continued for twenty-six hours: for the boiler test continuously; for the engine test at favorable times.

All observations were plotted, which presents an interesting study of the results and makes simultaneous readings possible with a limited corps of observers. The close agreement of these curves is a good check on the accuracy of the observations.

Time has not permitted the preparation of a complete report, but merely a summary of that portion of the test run at full speed under the most favorable conditions.

The horse power was determined by means of the Denny and Johnson torsion meter belonging to the United States steamship *Chester*, which was loaned by the Bureau of Steam Engineering, United States Navy Department, through the courtesy of Admiral Charles W. Rae, Chief of the Bureau. The details of the loan were arranged by Benjamin C. Bryan, Lieutenant Commander U.S.N., who gave the matter his personal attention and accompanied our party on the test.

The torsion meter was set up in the engineering laboratory and a thorough working knowledge obtained by the use of experimental apparatus before installing the meter on board. Thirty-six feet on the side shafts, and 49 on the centre shaft between inductors, was the greatest length obtainable, which gave a meter reading of about .50 and .73, respectively, at full power.

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[1] Reprinted from Transactions of the Society of Naval Architects and Marine Engineers, 1907, 15, 117–120, plates 37–39. Copyrighted.

In computing the horse power, 1.506, based on an assumed torsional modulus of elasticity of 11,600,000, was used for the constant K in the formula:

$$\text{H.P.} = \frac{Kd^4rR}{CL},$$

in which d = diameter of shaft in inches (6⅜).
r = torsion meter reading.
R = revolutions per minute

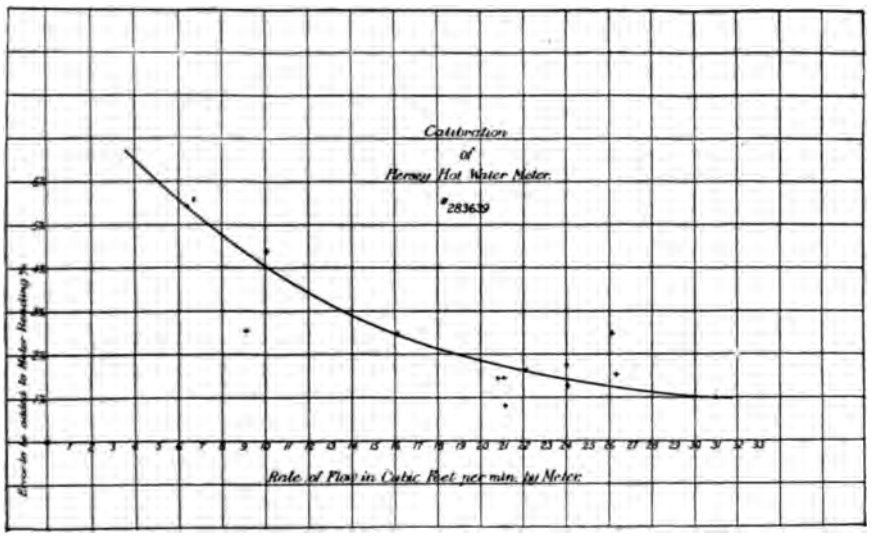

FIG. 1

C = inductor constant (12.5).
L = length of shaft in feet between inductors.

The water consumption was measured by a Hersey hot water meter, loaned by the Hersey Manufacturing Company, of South Boston. It was installed in the suction line between the hot well and the feed pump, and gave exceedingly satisfactory results.

This meter was later calibrated under similar conditions, the curve in Figure 1 showing the percentages of error. The plot of meter readings was struck in as a straight line, showing practically a uniform rate of water consumption, no point varying from the line by a quantity greater than 1 per cent. of the total.

The steam for all auxiliary purposes was passed through the two

auxiliary lines, one on each side of the vessel, and the quantity measured by its flow through orifices. A thin steel plate, having a hole $1\frac{5}{16}$ inches in diameter, was inserted in each auxiliary line between two flanges near the boiler. Pressures were read simultaneously at both orifices and at no time showed a variation of over a pound after making the proper gauge corrections.

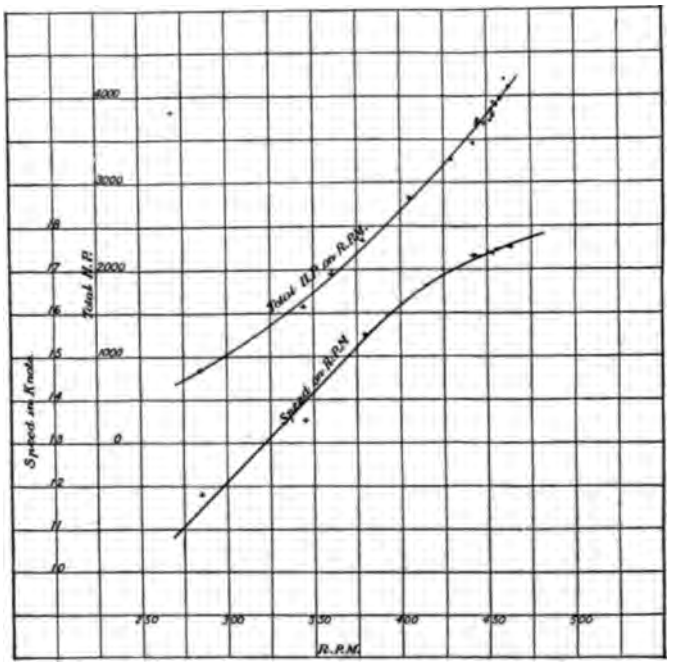

FIG. 2

The orifice was afterwards set up in the laboratory and its coefficient carefully determined by actually weighing the condensed steam under conditions similar to those on the boat.

Several buckets of coal were weighed, and their average, which varied only ten pounds from either maximum or minimum, multiplied by the number of buckets was taken as the coal consumption. The plot of coal consumption, like that of the water, is a perfectly straight line, showing a uniform rate.

The run from Boston to Portland was largely consumed in a progressive trial, the speed being taken by a stop-watch and a McGray electric

log towed from the end of a boom well clear of the wake. The log had previously been calibrated by towing over the measured mile.

Results of speed and power are shown in the curves in Figure 2.

The best run was made at full speed between Portland and Lubec, under the most favorable conditions of weather and sea. All observations were taken at ten-minute intervals excepting the coal, which was

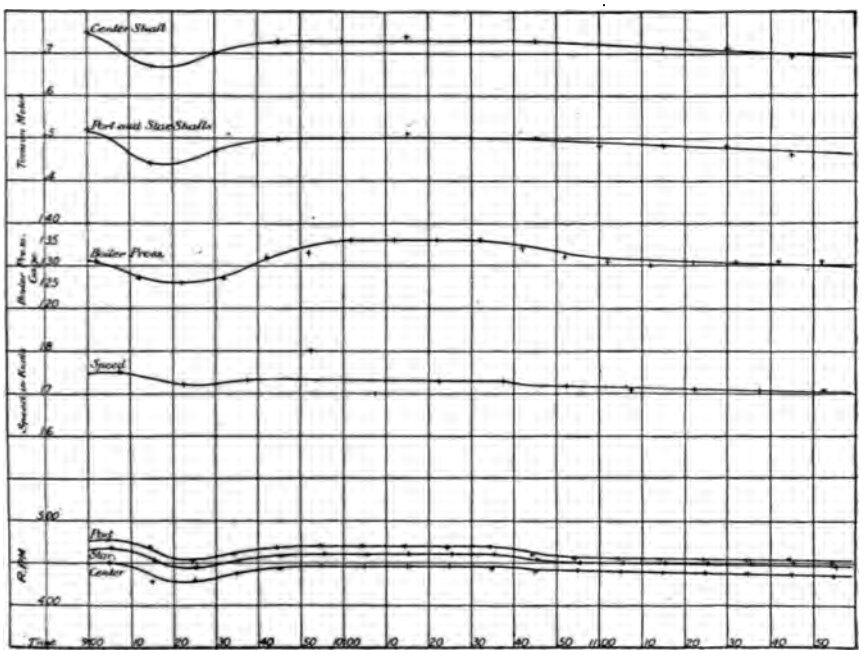

FIG. 3

recorded every fifteen minutes. Figure 3 shows the chief records during this test.

An attempt was made to determine the quality of steam, but as there were objections to tapping the main pipe a sample was taken from the drip connection which showed 2.5 per cent. of moisture, which is more than would be obtained from a fair sample.

It may be of interest to compare the following tabulated results with similar results obtained from a test on the steamship *Nantucket*, of the Merchants' and Miners' Transportation Company.

RESULTS OF TEST

	Nantucket.	*Cobb.*
Type of engine	Reciprocating	Parson's Turbine
Date of test	February 7, 1904	April 18, 1907
Duration of test — boiler	20½ hrs.	8 hrs.
Duration of test — engine	20½ hrs.	4 hrs.
Boiler pressure (average gauge)	147.3 lbs.	128 lbs.
Vacuum in inches	25	27
Quality of steam (sampled at drip)	98.8	97.3
Barometer	14.7 lbs.	14.7 lbs.
Temperature of air pump discharge	. .	110° F.
Temperature of feed water	209°.4 F.	213° F.
Kind of coal used	Georges Creek	Cape Breton
Moisture in coal	2.0%	1.9%
Ash and clinker in coal	7.6%	6.8%
Draft at blowers	Natural	2.1 in.
Number of boilers (single-ended Scotch)	4	6
Total grate surface	320 sq. ft.	323 sq. ft.
Total heating surface, approximately	10,150 sq. ft.	12,000 sq. ft.
Coal fired per hour	5,135 lbs.	8,050 lbs.
Water fed per hour (average during engine test),	45,844 lbs.	85,710 lbs.
Coal burned per square foot grate surface	16 lbs.	24.64 lbs.
Maximum revolutions	. .	p. 475, S. 460, C. 450
Corresponding total shaft horse power	. .	4,100
Average revolutions	74.05	447
Average total horse power	2,362 I. H. P.	3,747 S. H. P.
Steam for auxiliaries	. .	38,360 lbs.
Steam per I. H. P. per hour, total	19.41 lbs.	. .
Steam per shaft horse power per hour for all purposes	. .	22.67
Steam per shaft horse power per hour (propelling machinery only)	. .	19.74 lbs.
Speed (average)	15.00 k.	17.21 k.

DIMENSIONS

	Nantucket.	*Cobb.*
Length between perpendiculars	274 ft.	290 ft.
Beam molded	42 ft.	51 ft.
Draught	15 ft.	13 ft.
Displacement	2,700 tons	. .

ON THE FREE ENERGY OF NICKEL CHLORIDE[1]

BY M. DE KAY THOMPSON AND M. W. SAGE

I. INTRODUCTION

IN a previous paper[2] by one of the authors, calculations of the free energy have been made, from potential measurements, of all compounds for which the necessary data already existed, but so far no direct free energy determinations of salts have been made on the principle underlying these computations. The object of the following investigation is to determine the free energy of nickel chloride by this method, for a full description of which reference may be made to the above paper. Briefly, for the salt here investigated it consists in measuring the electromotive force of the cell:

$$\text{Nickel} \mid \text{Saturated solution of } NiCl_2 \mid Pt + Cl_2.$$

If the salt contained no water of crystallization and the chlorine were at a pressure of 76 cm. of mercury, the free energy increase of one mol of the salt would be,

$$\Delta F = -2EF$$

where E is the measured electromotive force and F is one faraday.[3] On account of the fact, however, that nickel chloride takes on water of crystallization, a slight modification of the ideal process by which the nickel and chlorine are allowed to unite reversibly is necessary.

Nickel chloride, in contact with water, forms the hydrate $NiCl_2.6H_2O$.[4] A hydrate with four mols has also been detected,[5] but this existed in contact with a saturated solution at a temperature about 80°, and conse-

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[1] Reprinted from the Journal of the American Chemical Society, 30, No. 5. May, 1908.

[2] Jour. Am. Chem. Soc., 28, 731 (1906).

[3] To bring the conception of free energy increase into conformity with the present more general usage, the terms involving RT are included in ΔF. See Haber, Thermodynamik technischer Gasreaktionen, p. 9.

[4] Lescœur, Ann. chim. phys. [6], 19, 533 (1890).

[5] Etard, *Ibid.* [7], 2, 545 (1894).

quently would not enter into this process. According to Lescœur, the anhydrous salt is produced directly on dehydrating that with two mols of water. This conclusion is based on vapor pressure measurements at 100°, starting with $NiCl_2.2H_2O$ and making measurements after successive evacuations of the apparatus. The final analysis of the hydrate gave $NiCl_2.1.45H_2O$, which might be a mixture of $NiCl_2.2H_2O - NiCl_2.1H_2O$ or $NiCl_2.2H_2O - NiCl_2$. Although this point is doubtful, it will be assumed that there is no hydrate with one mol of water.

The salt in contact with the saturated solution of nickel chloride is then $NiCl_2.6H_2O$, and in the ideal process, as nickel and chlorine unite and precipitate from the solution, water would be removed from the solution, and in order to keep the amount of water in the solution constant, this has to be supplied reversibly and isothermally at the same rate at which it is removed. This may be accomplished by means of isothermal distillation, as follows: Consider water at the temperature in question enclosed in a cylinder with a frictionless piston. Allow six mols to evaporate reversibly and isothermally. The free energy increase of the system is $-6RT$. Now separate the six mols and allow them to expand reversibly and isothermally until the pressure is equal to the vapor pressure of a saturated solution of $NiCl_2.6H_2O$. The free energy increase of the system in expansion is

$$-6RT\log\frac{p_{H_2O}}{p_{sol}},$$

if p_{H_2O} is the vapor pressure of water at T° absolute and p_{sol} is the vapor pressure of the solution. The water vapor may now be condensed reversibly into the solution at the same rate at which it is removed by the salt crystallizing out. The free energy increase of the system in this last step is $+6RT$, so that the net result is the free energy increase, $-6RT\log\frac{p_{H_2O}}{p_{sol}}$.

$$\Delta F_1 = -2EF - 6RT\log\frac{p_{H_2O}}{p_{sol}} \qquad (1)$$

is, therefore, the free energy of $NiCl_2.6H_2O$ referred to gaseous chlorine at atmospheric pressure and liquid water, both at T° absolute.

The free energy of $NiCl_2.2H_2O$ may be obtained from this by allowing $NiCl_2.6H_2O$ to change reversibly into $NiCl_2.2H_2O$ and four mols of liquid water. To do this allow four mols of water to evaporate

at the vapor pressure p_1 of the system $NiCl_2.6H_2O - NiCl_2.2H_2O$, whereby ΔF is $-4RT$. The water vapor must now be compressed to the vapor pressure p_{H_2O} of water, in which process ΔF is

$$+ 4RT \log \frac{p_{H_2O}}{p_1}.$$

The water vapor is then condensed to liquid water, in which ΔF is $+ 4RT$.

The free energy increase then of $NiCl_2.2H_2O$ is

$$\Delta F_2 = - 2E_F - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1}. \qquad (2)$$

By an exactly similar process the free energy increase caused by $NiCl_2.2H_2O$ going over to $NiCl_2$ and $2H_2O$ is

$$+ 2RT \log \frac{p_{H_2O}}{p_2},$$

where p_2 is the vapor pressure of the system $NiCl_2.2H_2O - NiCl_2$, and hence the free energy increase of formation of $NiCl_2$ is

$$\Delta F = - 2E_F - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1} +$$

$$2RT \log \frac{p_{H_2O}}{p_2} = - 2E_F + RT \log \frac{(p_{sol})^6}{p_1^4 p^2}. \qquad (3)$$

To all the above expressions a small correction must be made for the gaseous chlorine, whose pressure will, in general, not be 76 cm. of mercury. Assuming the vapor pressure of the solution to be unaffected by the presence of the chlorine in the enclosed space above, the chlorine couple[1] would be $b - p_{sol}$ where b = barometric pressure. The increase in free energy of the system when the chlorine expands from 76 cm. to $b - p_{sol}$ is

$$\Delta F = - RT \log \frac{760}{b - p_{sol}},$$

which must be added to the right-hand side of equation (3).

II. Potential Measurements

The apparatus in which the potential measurements were carried out consisted of an H-tube, 15 cm. high, with a glass stopcock in the

[1] See Jour. Am. Chem. Soc., 28, 733.

horizontal arm. The tubes of the vertical arms were 2 to 3 cm. in diameter. The stopcock was not lubricated and the potential of the cell was usually measured with the stopcock turned off.

The chlorine electrode was a smooth sheet of platinum with 10 per cent. iridium, 10 cm. long by 3 cm. wide. This was half way immersed in the solution, and chlorine gas, generated by the electrolysis of strong hydrochloric acid, bubbled over it from below. The chlorine was led from the cell by a rubber tube to a bottle containing potassium hydroxide, where it was absorbed. The pressure of the gas over the chlorine electrode was determined by a small manometer in the escape tube and by the barometer reading. The nickel electrode was formed by electrolytic deposition of nickel on platinum or copper. It is known that nickel exists both in the active and passive states and that active nickel rapidly changes over to the passive state if exposed to the oxygen of the air. Pure nickel immersed in molal nickel sulphate gives about -0.2 volt,[1] while, according to Muthmann and Frauenberger,[2] active nickel has a potential of $+0.32$ volt. The nickel having this potential was prepared by electrolytic deposition on platinum "according to the directions for electro-analysis." This statement and that which follows later, according to which the solution used was neutral nickel sulphate and the impressed voltage 8 volts, are all the directions given for obtaining a nickel deposit giving the voltage quoted above. The first measurements of the nickel couple were attempts to reproduce this potential in a molal solution of neutral nickel sulphate. The measurements were made by the Poggendorf method with a Weston standard cell and Lippmann electrometer. The potential between the nickel sulphate and normal potassium chloride was eliminated by a saturated solution of potassium chloride or ammonium nitrate placed between the two.[3] The potential was measured within thirty seconds after plating. It was found that on electrolyzing a neutral sulphate solution at room temperature with 8 volts a green deposit appeared on the cathode whose potential was about that given by Muthmann and Frauenberger, and which decreased rapidly. On heating a solution containing 60 grams $NiCl_2.6H_2O$ per liter to 90° and electrolyzing with 12.5 volts, the nickel

[1] All single potentials in this paper refer to the "normal electrode" as -0.560 volt at 20°.

[2] Sitzungsber. kgl. Bayr. Akad. Wiss., 34, 201 (1904).

[3] Bjerrum, Z. physik. Chem., 53, 428 (1905).

came down in a black spongy form, and no green compound was visible. The highest potential obtained was +0.112 volt. Many other solutions were used, but none gave such high results as the neutral sulphate. For example, a solution containing 60 grams $NiSO_4.6H_2O$ + 20 grams $(NH_4)_2SO_4$ + 40 c.c. NH_4OH per liter, electrolyzed at 20° with 8 volts, gave a deposit of nickel whose potential was +0.017 volt. This was a gray, firm deposit, and could be easily duplicated. Our only explanation of Muthmann and Frauenberger's high value for nickel is that some of this green precipitate came down with the nickel. If this nickel was obtained in a cold solution with 8 volts, this is certain to have happened. The nickel deposits obtained in the hot solution did not maintain a constant voltage, but fell off as rapidly as in the case of the green precipitate obtained in the cold. Attempts to increase the voltage by polarizing with hydrogen were not successful. In preparing the nickel electrodes for the final measurements the anode and cathode were separated by the wall of a porcelain cup, and in all cases pure electrolytic nickel anodes were used. This cup was to protect the cathode from any sulphuric acid set free at the anode, as it was found, as stated by Muthmann and Frauenberger, that any free acid reduced the potential.

The actual measurement of the cell

Nickel | Saturated solution $NiCl_2.6H_2O$ | Pt + Cl_2

at 20° was now taken up. A saturated solution of the chloride was prepared by rotating bottles for several days in a thermostat maintained at 20° by means of a mercury regulator and electric lamps. The dissolved nickel was determined by electro-analysis, and three determinations gave 60.5, 60.6, and 60.9 grams of anhydrous salt per hundred grams of water. This is somewhat less than 64 grams chloride to 100 grams water as found by Etard.[1] The density of this solution referred to water at 4° was 1.474.

Before making measurements, chlorine was allowed to bubble over the platinum-iridium plate for an hour or so, so as to give the solution in this arm of the H-tube time to get saturated with chlorine and to drive out all air above the solution. After leaving the cell it was tested by absorbing in potassium iodide in an inverted test tube. The absence of bubbles showed the gas to be pure chlorine. The electromotive force of this couple was measured against the "normal electrode" and was

[1] Landolt-Börnstein-Meyerhoffer Tables, 3d edition, p. 562.

found to be — 1.59 volts. The nickel electrode was now prepared as described above and changed from the plating solution to the cell as quickly as possible and the reading on the bridge taken immediately. This could be done within thirty seconds from the time the plating was finished. Cleaning off the sulphate adhering to the electrode by dipping in water did not affect the result. The electromotive force of the cell thus measured varied between 1.65 and 1.707 volts, the latter being the highest value obtained in a large number of measurements. This, therefore, corresponds to the most active nickel obtained above. The pressure of the chlorine gas at the time of the latter measurement was 752 mm. mercury.

As there is approximately 0.2 volt difference between the highest value here obtained and that which would have resulted if the nickel couples had as high a value as that assigned them by Muthmann and Freuenberger, some decomposition point determinations of the saturated solution between small platinum plates were made for the purpose of determining whether the above measured value is reversible. The values obtained were not used for computing the free energy, but were simply to decide whether an error of 0.2 volt in the above value were possible. The values found were 1.61, 1.63, 1.60, and 1.60 volts. These are somewhat less than the highest value found above, but the agreement indicates that 1.7 volts and not 1.9 volts is the voltage of the cell.

III. Vapor Pressures

The vapor pressure of the saturated solution of nickel chloride has been found by Lescœur[1] to be 8 mm. Hg and that of the system $NiCl_2.6H_2O$ — $NiCl_2.2H_2O$ to be 4.6 mm. Hg, both at 20°. The system $NiCl_2.2H_2O$ — $NiCl_2$ was found to have a vapor pressure at 100° of 123 mm. No measurement is given of this quantity at 20°, but the statement is made that it is zero, which is, of course, impossible.

By means of the integrated van't Hoff formula this pressure could be calculated, however, from the pressure at 100° if the heat of hydration of $NiCl_2.2H_2O$ were accurately known. This is equal to the difference between the heat of hydration of $NiCl_2.6H_2O$ starting from $NiCl_2$ and from $NiCl_2.2H_2O$. The former quantity is 20,330 cal.[2]

[1] Ann. chim. phys. [6], 19, 533 (1890).

[2] Landolt-Börnstein-Meyerhoffer Tabellen, p. 461.

The following table shows the latter value, q, obtained from Lescœur's vapor pressure of the system $NiCl_2.6H_2O$ — $NiCl.2H_2O$ by the formula:

$$4.57 \log_{10} \frac{p_2}{p_1} = q\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

All except the last column are taken from Lescœur.

Temperature.	Pressure in mm. Hg.	q.
15°	3.4	10,540
25°	6.3	
20°	4.6	14,760
30°	10.5	
40°	24.0	14,000
15°	3.4	
30°	10.5	15,470
40°	24.0	

Subtracting the average value of q from 20,330, the heat of hydration of $NiCl_2.2H_2O$ is obtained. Computing this from the value of the vapor pressure of $NiCl_2.2H_2O$ at 20°, 11.5 mm. results, which is greater than that of $NiCl_2.6H_2O$, and is therefore impossible. It is evident, therefore, that this value of the heat of hydration is not accurate enough for this purpose.

The value of this pressure was obtained directly by the tensimeter method. For this purpose one tensimeter was filled in June and three in July.[1] One bulb contained phosphorus pentoxide and the other the salt. The liquid in the manometer was cottonseed oil of specific gravity 0.9185. The tensimeters were placed on their side, carefully pumped out, and at the same time warmed. They were then left several hours in connection with the pump and again pumped out and warmed before sealing off. In October they were placed in a thermostat at 20° and allowed to remain until January. The following table gives the readings in millimeters of oil:

[1] See Findlay, The Phase Rule, p. 88.

Date.	No. 1.	No. 2.	No. 3.	No. 4.
December 30	11.4	7.0	3.6	5.4
January 7	. .	6.3	broken	6.4
January 25	11.6	6.8	. .	6.1
Mol water to 1 mol salt	2.06	2.05	. .	1.99

December 30, after the measurements, the bulbs of Nos. 2 and 5 containing the $NiCl_2$ were placed in a beaker of hot water for a few minutes to see if the evolution of water vapor could not be accelerated. The pressure increased to 10 to 15 cm. of oil, due, evidently, to the expansion of water vapor already present, but went back to nearly the same values afterwards. The water in the salt in the tensimeters was determined by analyzing for the amount of nickel present subsequent to these measurements, and the results were those shown in the table above. It is evident from the above that No. 1 was not properly filled, and is therefore omitted in taking the mean. The average of Nos. 2 and 4 is 0.43 mm. of mercury.

In order to check this value by a different method it was decided to measure it at 110° and compute by the van't Hoff equation from this and from Lescœur's value at 100°, the value at 20°.

For this purpose a tensimeter was filled with some nickel chloride that had been in the drying closet for more than a week at 100°. Mercury was used in the manometer and phosphorus pentoxide in the drying bulb. It was first placed in a steam bath to see that it checked with Lescœur's value. The tensimeter was left at four in the afternoon, and next morning was found at 123 mm. Hg, reduced to 0°, at which pressure it remained constant for the following twenty-four hours. This agrees identically with Lescœur's value. It was then placed in a bath of vapor from boiling toluene and in a few hours reached a constant pressure of 218 mm. Hg at a temperature of 110.7°, as obtained from a thermometer corrected at this point by a standard from the Reichsanstalt. The value at 20° computed from this is 0.46 mm.

The tensimeter was then opened and heated while exhausted and connected to the air pump for an hour and a half at a temperature varying from between 90° and 120°, thereby driving off some water. It was sealed off while hot and again placed in the bath of toluene vapor. The constant pressure reached as before in a few hours was

216 mm. Hg at 110.6°. The pressure computed from this measurement for 20° is 0.47 mm.

These values agree well enough for the present purpose with the average of those from direct measurements. The best value to adopt is the average of the four, which is 0.45 of mercury. It is interesting to note that on cooling, the mercury in the tensimeter immediately goes back to nearly a zero pressure, showing that water is taken up by the chloride more rapidly than it is evolved.

Substituting in formula (3) $E = 1.71$ volts, $p_{sol} = 8.0$, $p_1 = 4.6$, and $p_2 = 0.45$, $\Delta F = -74{,}400$ cal. The correction due to the pressure of the chlorine not being 760 mm. is negligible.

The heat of the reaction, or the increase in total energy, is $-74{,}500$ cal., assuming the compound to be formed from gaseous chlorine. If the chlorine were solid and superheated to this temperature, the total energy increase is obtained by increasing the above value by the sum of the heat of fusion and the heat of vaporization of chlorine, which has been estimated at 7,000 cal.[1] This gives $-67{,}500$ cal. as the total energy change, starting with solid chlorine. Likewise, if the chlorine were solid the free energy increase ΔF would be diminished by the quantity RT, or approximately 600 cal., giving the value $F = -75{,}000$. The ratio of free to total energy for chlorine in the solid state consequently is 1.11, while the ratio of the same quantities with chlorine in the gaseous state is 1.00. The free energy and the total energy of this salt, therefore, are approximately equal, as was found to be true in all other cases for which this calculation has been made.

IV. Precision Discussion

The term $2EF$ in formula (3) amounts to 79,040 cal., the second term to only 4,600 cal., from which it is evident that even a large error in the vapor pressures would have only a relatively small effect on the final result. Assuming an error of 0.1 mm. in p_{sol}, p_2 and 0.1 mm. in p, which seems an outside limit, the resultant effect is 600 cal., or about 0.8 per cent. error in ΔF. Assuming a possible error of 0.02 volt in E the combined error in ΔF would be 990 cal., or 1.3 per cent.

[1] Jour. Am. Chem. Soc., **28**, 741 (1906).

V. Summary

The free energy ΔF of $NiCl_2$ was determined by measuring the potential of the cell.

Ni | Saturated solution of $NiCl_2.6H_2O$ | Cl_2 + Pt.

A formula for ΔF was deduced, involving this potential, the vapor pressure of the saturated solution of the system $NiCl_2.6H_2O$ – $NiCl_2.2H_2O$ and of $NiCl_2.2H_2O$ – $NiCl_2$. The pressure of the last system was obtained both by direct and by indirect measurement. The free energy and total energy of $NiCl_2$ were found to be approximately equal.

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THE COLORED SALTS OF SCHIFF'S BASES—A CONTRIBUTION TO OUR KNOWLEDGE OF COLOR AS RELATED TO CHEMICAL CONSTITUTION[1]

By F. J. MOORE and R. D. GALE

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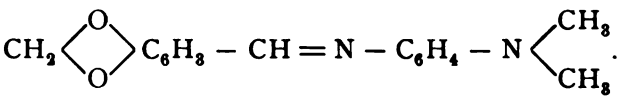
I. The Hydrochlorides of Bases Formed by Condensing *p*-Amino Dimethylaniline with Aromatic Aldehydes

The starting point of the present investigation was a chance observation made upon the compound produced by condensing *p*-aminodimethylaniline with piperonal. This product is of a light orange color and has the formula,



When this substance, either in the dry state or in ethereal or benzene solution, is treated with dry hydrochloric acid gas, one molecule of the latter is first added to form a salt of a deep blood-red color. This salt can further add another molecule of the acid to form a dihydrochloride. The color of the latter salt, in sharp contrast to that of the former, is a bright lemon-yellow.

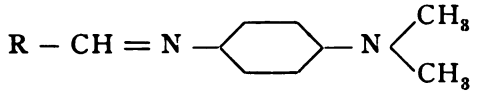
We found this phenomenon so striking that we determined to prepare a number of compounds of analogous constitution and study the color of their salts. The first substances selected were those most strictly analogous to the one already mentioned, namely; the condensation products of *p*-aminodimethylaniline with aromatic aldehydes. These bases furnish the subject-matter of the present paper. They all show a behavior toward hydrochloric acid, and (so far as has been tested) also toward other acids, entirely analogous to that described in the case of the piperonal compound. A minor exception has to be noted in the case of anisaldehyde. When its condensation product with *p*-aminodimethylaniline is treated with hydrochloric acid, the same color changes are observed as in the other cases, but analysis of the products shows

[1] Reprinted from the Journal of the American Chemical Society, 30, No. 3, March, 1908.

that a maximum of nearly three molecules of the acid is here absorbed. This behavior will be discussed more fully in the experimental part.

Subsequent papers will deal with other compounds similarly constituted. Thus we have prepared a number of bases of this class by condensing aromatic aldehydes with *p*-aminodiethylaniline. Of these it may be said that as far as investigated they show the same reactions toward acids as the corresponding dimethyl compounds. The salts are, however, less stable. One of us, in collaboration with Mr. R. G. Woodbridge, Jr., is also studying the bases formed by condensing *p*-aminodiphenylamine with aldehydes.

From the above it is clear that we are dealing with a quite general law, which may be stated thus: Bases of the general formula,



add hydrochloric acid to form salts of a dark red color (darker than that of the free base), while most of them also add another molecule of the acid to form salts of a light yellow color (usually lighter than that of the free base).

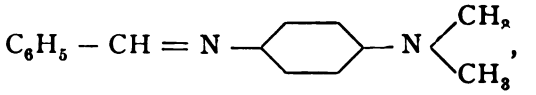
Before attempting a theoretical explanation of this uniform behavior, a word should be said concerning the color of the simpler benzylidene compounds containing only one atom of nitrogen. As aromatic aldehydes condense so readily with primary amines, a voluminous literature has grown up on the subject. We have not made an exhaustive study of this, but the general rule seems to be that neither such bases nor their salts are very highly colored. This certainly holds true of those which have come under our observation. Thus the condensation product of benzaldehyde with aniline is a pale cream color (perhaps due to a trace of impurity), and the product formed by treating piperonal with aniline is perfectly colorless. The hydrochloride of the piperonal compound is a bright lemon-yellow; that of the benzaldehyde compound a much paler shade, only slightly stronger than that of the free base. For purposes of comparison we have prepared several other condensation products of piperonal. All of these, namely, the compounds prepared by treating piperonal with *p*-toluidine, *p*-chloraniline, *p*-bromaniline, *p*-aminoethylbenzoate, and *m*-nitraniline, all showed the same light color of base and salt.

From this we can draw the conclusion that if the group $-CH=N-$ is to be considered a chromophore at all, it is a weak one; certainly far

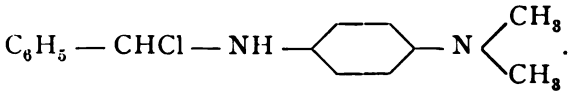
weaker than $-N=N-$. Of the intensifying effect of acid addition or salt formation, whether we call it "auxochrome" effect or "halochromy," we may say that in this group of compounds it is noticeable but not striking.

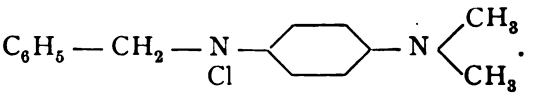
Turning back now to the more complicated bases containing two atoms of nitrogen, inspection of their formulæ shows the presence of the substituted amino group, $-N\langle^{CH_3}_{CH_3}$, which acts as an auxochrome in so many important dyes. The effect of this group is seen in the color of the bases which contain it. These colors range from a light yellow, through golden yellow, to a fairly strong orange. None go as far as deep red. The color of the salts has already been dwelt upon.

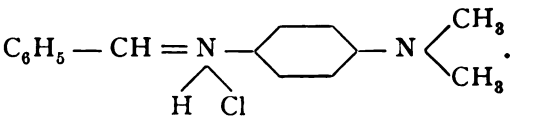
Our interpretation of the color relations so frequently referred to will depend upon our idea of exactly what happens when one molecule of hydrochloric acid is added to these bases. If we take for purposes of illustration the simplest case, that of benzylidene *p*-aminodimethylaniline,

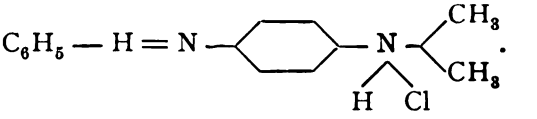


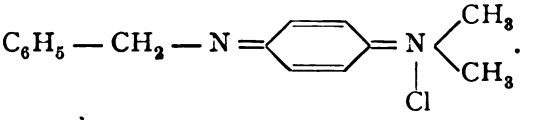
we can imagine hydrochloric acid being added to the compound in such different ways as to form products of any one of the following formulæ:

(1) 

(2) 

(3) 

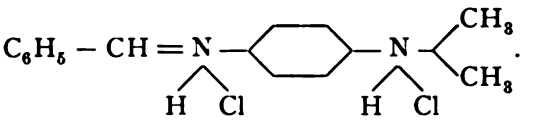
(4) 

(5) 

Of these, (1) and (2) seem hardly worthy of serious consideration. The addition products of acids to the simpler bases of this type, such as benzylidene aniline, $C_6H_5 - CH = N - C_6H_5$, have always been looked upon as ammonium salts. They split at once under the influence of water into the corresponding aldehyde and the salt of the base from which they were originally formed — in this case, aniline hydrochloride and benzaldehyde. The salts of the more complicated compounds now under discussion act in a similar way. This would exclude (1). It would not necessarily exclude (2), according to which the addition products are to be looked upon as secondary chloramines. They are, however, rather more stable than chloramines would be expected to be, and they do not evolve chlorine when they are treated with hydrochloric acid. A more conclusive argument, however, against (1) and (2), and in favor of the salt-like character of the compounds, is the fact that so far as tested (and only qualitative tests have thus far been made) sulphuric acid gives addition products entirely similar in color and properties to those formed by hydrochloric acid.

Formulæ (3) and (4) represent more nearly what we should expect if the addition of hydrochloric acid is to be looked upon as simple salt formation. The formulæ differ only in the nitrogen atom, which is supposed to become pentavalent. In deciding between them we have to remember that the simpler bases, like piperonylidene aniline, add one molecule of hydrochloric acid to form salts which are not dark red but light yellow. Now these salts must have their hydrochloric acid united to that nitrogen which forms part of the chain connecting the two benzene rings. It would therefore seem quite probable that these red salts have their hydrochloric acid bound differently. Furthermore, if we assign to the red salt the formula (4), a consistent and plausible explanation lies near at hand for the difference in color between the salts containing one and two molecules of hydrochloric acid, respectively. In the first case, we have three factors coöperating to intensify the color, the chromophore group, $-CH = N -$, the auxochrome group, $N\langle^{CH_3}_{CH_3}$, and, finally, whatever influence in this direction is to be ascribed to salt formation — "halochromy."

Now the compound with two molecules of hydrochloric acid can hardly have any other formula than the following:



Here the nitrogen belonging to the chromophore group, $-CH=N-$, has changed its valence, and this might naturally be expected to prove destructive to the chromophore character of the group. Furthermore, the light yellow color of these saturated salts is in entire harmony with the similar color of the simpler bases which, as already pointed out, must have the hydrochloric acid upon the central nitrogen.

An argument against the explanation just outlined might be found in the hydrolysis of the salts. It is a well-known fact that the salts of the simpler bases, like benzylidene aniline, decompose at once when treated with water, yielding in this case aniline hydrochloride and benzaldehyde. The salts of the more complicated bases we are studying react similarly, except that the operation takes place in two steps. If the yellow hydrochloride of piperonylidene *p*-aminodimethylaniline, for example, be treated with water, it immediately turns dark red, obviously owing to the formation of the red monohydrochloride. The color then slowly fades out as this salt splits into the hydrochloride of *p*-aminodimethylaniline and piperonal. Now the weak spot in the hydrochloride of piperonylidene aniline is obviously the molecule of acid attached to the central nitrogen. If the red salt has then a constitution analogous to that shown in formula (4), it is not, at first sight, quite clear why it should hydrolyze at all. The above argument, however, against (4) does not seem as serious as that which can be brought against (3). If we give the latter formula to the red hydrochloride, we can only ascribe the intensity of its color to salt formation — halochromy. We should then expect a further intensification of the color when the second molecule of hydrochloric acid is added. As we have already seen, this is not the case.

There remains the quinoid formula, (5). This also offers a consistent explanation. We have only to assume that the red hydrochloride exists in the quinoid, the yellow dihydrochloride in the benzoid form. It seems at first a little difficult to account for the hydrolysis into aldehyde and amine salt on this basis, but the shifting of double bonds involved is not of a particularly revolutionary character. It would also seem possible that the dihydrochlorides might also exist in a quinoid form. Perhaps when more compounds have been studied such salts

will be found. In the meantime, some work is under way in this laboratory designed to throw light upon the probability of a quinoid formula for the red hydrochlorides.

An explanation, differing from any of the above, has occurred to us since reading a recent article by Anselmino[1] which came to our notice after the experimental work described in this paper was practically completed. Anselmino found that when *p*-homosalicylic aldehyde is condensed with aniline the product formed exists in two different forms, a red and a yellow. That this is not simply a case of dimorphism is shown by the fact that the two forms differ in chemical behavior and give different derivatives. The most probable assumption concerning their constitution would seem to be that they are stereoisomeric in the same sense as the isomeric oximes of unsymmetrical ketones. If we try to explain the behavior of the compounds we are studying upon a similar basis, we should have to say that the salts vary in color because they are derived from different stereoisomeric bases, one red, the other yellow; that in the case of the bases themselves, the yellow form is alone stable; that when the bases add hydrochloric acid, the yellow salts first formed are unstable and go over to form salts of the other — red base; finally, when the saturated salts are formed, that a transformation in the opposite sense takes place. This explanation disregards the question as to which nitrogen holds the hydrochloric acid. Now, in this connection, we have to remember that previous to this recent work of Anselmino, no well-attested cases of stereoisomerism had been observed among benzylidene compounds, though they have long been looked for; and, further, that Anselmino himself observed no such isomerism in the case of the salts. In fact he points out that his red and yellow bases gave identical hydrochlorides. This, of course, is no conclusive argument against a stereochemical explanation of the facts which we have observed. It does, however, furnish a reason for not accepting such an explanation hastily.

It will be seen in the experimental part of this paper that the salts of salicylidene *p*-aminodimethylaniline undergo change in color on standing, and it has been already pointed out that compounds of this class containing the diethylamino group show similar behavior. From what has already been said, it will be seen in what a variety of directions an explanation of this fact might be sought. Any discussion of these

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[1] Ber., 40, 3465 (1907); also *Ibid.*, 38, 3989 (1905).

possibilities would, however, be premature until more work upon these ethyl compounds has been done. For the present also we wish to reserve any opinion as to the probable formulæ of the red hydrochlorides.

Experimental Part

The condensation product of *p*-aminodimethylaniline with benzaldehyde was first prepared by Calm.[1] It is interesting to note his observation that this base adds two molecules of hydrochloric acid to form a "white" salt. This illustrates the light color of the saturated hydrochloride, and at the same time shows that Calm attached no significance to the formation of the red intermediate product. He gives a determination of chlorine in the saturated salt. The other bases studied in this paper were prepared by Nuth[2] at the suggestion of Calm. He did not prepare salts. We have little to add to his description of the bases, except for some melting points already corrected by more recent observers. We prepared the bases by mixing molecular quantities of the amine with the various aldehydes, sometimes warming a little on the water bath. The reaction then proceeded at once and gave good yields. The product was recrystallized once from alcohol. It was usually found that further recrystallization did not raise the melting point. The bases range in color from a light yellow to a light orange.

In studying the salts we at first allowed hydrochloric acid to act upon the bases in the dry state. When piperonylidene *p*-aminodimethylaniline, for example, is spread upon a piece of porcelain (a crucible cover) and a current of hydrochloric acid passed over it, the mass suddenly turns a deep red. This color no sooner appears than it begins again to fade, owing to the formation of the light yellow saturated salt. A similar effect is produced when the base is dissolved in dry ether and hydrochloric acid gas introduced. Here the liquid first turns dark red; then a precipitate of the same color appears, and finally, the time varying with the amount of substance present, the color of the solution grows rapidly lighter in shade, the precipitate becomes bright yellow, and at the end the supernatant liquid is colorless, the saturated salt being practically insoluble in ether. It will frequently be noticed that at the mouth of the tube where the gas enters, and where consequently the acid is always in excess, a yellow deposit of the dihydrochloride

[1] Ber., 17, 2938 (1884).

[2] *Ibid.*, 18, 573 (1885).

forms at once. This makes it probable that the red salt, however it is prepared, contains a good deal of the yellow enclosed. This shows itself in the analytical data furnished further on. When the salts were prepared for analysis, the following procedure was employed in order to avoid this kind of contamination as much as possible. First, the free base was dissolved in sodium-dried ether, and then a solution of hydrochloric acid in dry ether was run in from a burette. When preparing the saturated salt, the addition of the acid solution was continued as long as any precipitate formed. To prepare an unsaturated salt, a little less than half as much acid was added as had been found necessary in preparing the saturated one. The precipitates so obtained were filtered by suction, washed repeatedly with dry ether, and finally dried in a vacuum desiccator containing both concentrated sulphuric acid and sticks of caustic soda. If lumps formed during the drying, these were ground up and the desiccation continued. As far as our observation goes, these salts melt only with decomposition, and the temperature observed depends largely upon the time of heating. In the case of the saturated salts, the point of decomposition lies quite close to 200° in almost all cases. The chlorine determinations were in all cases made by the Carius method. The salts precipitated and dried as above described were used for analysis without recrystallization. Alcohols would have been the only practicable solvents for this purpose, but some experiments made in this direction led us to fear the contaminating effects of hydrolytic action. As we have pointed out above, the salts were probably more or less contaminated with each other, and perhaps also with the free bases. Under the circumstances we have not thought it desirable to make a large number of determinations, in the hope that some of them might agree more closely with the results of theoretical computation. In spite of the wide divergence to be observed in many cases, we think that the numerical results make plain the one point which we wish to emphasize at this time, namely, that the light-colored salts contain about one molecule of acid more than the dark ones. The results follow:

Benzylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{15}H_{16}N_2.HCl$, Cl, 13.60; found, 17.01. Saturated hydrochloride: calculated for $C_{15}H_{16}N_2.2HCl$, Cl, 23.09; found, 20.48.

Cinnamylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{17}H_{18}N_2.HCl$, Cl, 12.36; found, 15.33. Saturated hydrochloride: calculated for $C_{17}H_{18}N_2.2HCl$, Cl, 21.95; found, 21.34.

Piperonylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{16}H_{16}O_2N_2.HCl$, Cl, 11.63; found, 15.19. Saturated hydrochloride: calculated for $C_{16}H_{16}O_2N_2.2HCl$, Cl, 20.78; found, 21.12, 21.05.

Salicylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{15}H_{16}ON_2.HCl$, Cl, 12.81; found, 13.07. Saturated hydrochloride: calculated for $C_{15}H_{16}ON_2.2HCl$, Cl, 22.65; found, 22.47.

The color of the salts seemed less permanent in this case than in any we had previously studied. Nuth records that the free base turns red on standing in the air, and we notice that the red hydrochloride has a tendency to grow lighter in color. What is perhaps more curious is that the saturated hydrochloride, which when first precipitated is almost colorless, grows considerably darker in color. We have since met with even more marked changes of this kind in the study of the bases formed by condensing *p*-aminodiethylaniline with aldehydes. We consider any theoretical discussion of this phenomenon to be premature until these diethyl compounds have been more thoroughly studied. The fact should be borne in mind, however, that, according to Anselmino, salicylic aldehyde is one of those which forms isomeric aniles, one red, the other yellow.

Anisylidene p-Aminodimethylaniline. — Red hydrochloride: calculated for $C_{16}H_{18}ON_2.HCl$, Cl, 12.20; found, 12.20. $C_{16}H_{18}ON_2.2HCl$, Cl, 21.68; found, 18.34. Saturated hydrochloride: calculated for $C_{16}H_{18}ON_2.3HCl$, Cl, 29.27; found, 28.78, 26.16, 26.61.

In view of the fact that in the case of the red hydrochlorides high results for chlorine are usually obtained, probably owing to the tendency of these salts to enclose some of the saturated compounds, the numerical results given above leave it a little in doubt whether the red salt in this case contains, when pure, one or two molecules of acid. It is quite evident, however, that the saturated salt contains nearly three molecules. This seems to be one of those cases referred to by Baeyer[1] where a base shows itself capable of combining with more acid than its formula accounts for. It might be supposed that in both salts the additional molecule of hydrochloric acid attached itself to the methoxyl group to form an oxonium salt. This may be the correct explanation, but it is not necessarily so; for we find that the most simply constituted member of the whole group, benzylidene aniline, though it contains but one

[1] Ber., 38, 1157 (1905).

nitrogen and no oxygen, yet adds two molecules of hydrochloric acid, as shown by the following analysis:

Calculated for $C_{18}H_{11}N.HCl$, Cl, 16.29; for $C_{18}H_{11}N.2HCl$, Cl, 27.90; found, 27.68, 27.62.

We were much surprised at this result, as it raised the question whether all of the benzylidene compounds containing one nitrogen might not behave similarly, and whether in those containing two atoms all of the acid might not be held by one nitrogen. The analyses of the salts of the three following compounds, however, show that the addition of more molecules of acid than there are nitrogen atoms in the base is the exception; though from what has gone before, it may well be of more frequent occurrence than has hitherto been supposed.

Piperonylidene Aniline. — This base was first prepared by Lorenz.[1] It is absolutely colorless, the first of these compounds which we have been able to prepare in that condition. The hydrochloride is bright yellow, and this makes perhaps the most striking example of simple "halochromy" which we have observed in the group. The hydrochloride contains but one molecule of acid, as is shown by the following analytical data:

Calculated for $C_{14}H_{11}O_2N.HCl$, Cl, 13.55; found, 13.76, 13.51.

Piperonylidene p-Toluidine. — This substance crystallizes from alcohol in cream-colored prisms which melt at 98°.

Calculated for $C_{15}H_{13}O_2N$, C, 75.26; H, 5.48; N, 5.87; found, 75.28, 5.55, 6.11.

The hydrochloride is light yellow. The percentage of chlorine was determined. Calculated for $C_{15}H_{13}O_2NHCl$, Cl, 12.86; found, 13.03, 12.98.

Piperonylidene p-Chloraniline. — The base melts at 78°. It has not been analyzed. It forms a light yellow hydrochloride. Calculated for $C_{14}H_{10}O_2NCl.HCl$, Cl, 23.95; found, 23.43.

We wished to learn something of the color of salts analogous to those formed by condensing aldehydes with *p*-aminodimethylaniline, but which contained an amino group not substituted by alkyl radicals. We had some hopes that at least a small yield of such compounds might be obtained by condensing one molecule of aldehyde with one of a diamine. Accordingly we treated piperonal with *p*-phenylenediamine, and also with benzidine. In both cases the only products we obtained were those

[1] Ber., 14, 792 (1881).

formed by the condensation of one molecule of diamine with two molecules of piperonal. These bases are soluble with difficulty in alcohol, ether, or the aromatic hydrocarbons. They can be crystallized from nitrobenzene, from which they separate in bronze yellow scales of a semi-metallic luster. The compound with *p*-phenylenediamine melts at 216°. Calculated for $C_{22}H_{16}O_4N_2$, C, 70.94; H, 4.33; N, 7.55; found, 70.30, 4.52, 7.90.

The compound formed by condensing benzidine with piperonal melts not quite sharply at 241°. The liquid formed is not transparent, and it is possible that it is crystalline in character, as liquid crystals are not infrequently met with among compounds of similar constitution. The composition of the base was verified by a nitrogen determination. Calculated for $C_{28}H_{20}O_4N_2$, N, 6.50; found, 6.43.

We add some incomplete data concerning some substances prepared during the present investigation, but which, as they have no further theoretical interest for us, will probably not be worked with further.

Piperonylidine p-Aminoethylbenzoate. — This substance was prepared by condensing piperonal with *p*-aminoethylbenzoate. The base melts at 109°, is almost colorless, and forms a yellow hydrochloride.

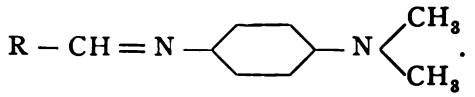
Calculated for $C_{17}H_{15}O_4N$, C, 68.64; H, 5.09; N, 4.72; found, 68.34, 5.08, 4.84.

Piperonal condenses readily with *m*-nitraniline to form a base which melts at 119°. This forms a yellow hydrochloride. We have a nitrogen determination in the free base. Calculated for $C_{14}H_{11}O_4N_2$, N, 10.35; found, 10.56.

Piperonal condenses with *p*-bromaniline to form a product melting at 109°. This forms a hydrochloride of a light canary-yellow color. We have analyzed neither the base nor the salt.

Summary

When *p*-aminodimethylaniline is treated with aromatic aldehydes, condensation products are formed which have the general formula,



These bases add one molecule of hydrochloric acid to form dark red salts of a much deeper color than the free bases. The addition of more hydrochloric acid produces salts of a light yellow color, lighter than that of the free base.

Three explanations of this behavior are considered:

(1) That the first molecule of acid adds to the auxochrome nitrogen augmenting the color, while the second adds to the chromophore nitrogen, changing its valence and consequently destroying its chromophore character.

(2) That the monohydrochloride has a quinoid structure, while the saturated salt and the free base are benzoid.

(3) That there is a double series of stereoisomeric red and yellow bases and salts, the red form of the monohydrochloride being the stable one, the yellow form being stable in the other cases.

A decision as to which of these explanations is most applicable must be deferred until more experimental material can be collected.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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CONTRIBUTIONS FROM THE
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No. 29

A REVISION OF THE FUNDAMENTAL LAWS OF MATTER AND ENERGY

BY GILBERT N. LEWIS

RECENT publications of Einstein[1] and Comstock[2] on the relation of mass to energy have emboldened me to publish certain views which I have entertained on this subject and which a few years ago appeared purely speculative, but which have been so far corroborated by recent advances in experimental and theoretical physics that it seems desirable to subject these views to a strict logical development, although in so doing it will be necessary to modify those fundamental principles of the mechanics of ponderable matter which have remained unaltered since the time of Newton.

The recent experiments which indicate a change in the mass of an electron with the speed, together with the phenomenon of radio-activity, have in some minds created a doubt as to the exact validity of some of the most general laws of nature. In the following pages I shall attempt to show that we may construct a simple system of mechanics which is consistent with all known experimental facts and which rests upon the assumption of the truth of the three great conservation laws, namely, the law of conservation of energy, the law of conservation of mass, and the law of conservation of momentum. To these we may add, if we will, the law of conservation of electricity.

THE RELATION OF MASS TO ENERGY

When a black body[3] is placed in a beam of light it is subject to a pressure or force which tends to move it in the direction in which the light is moving. If $\frac{dE}{dt}$ denotes the time rate at which the body

[1] Ann. Phys., 18, 639 (1905).

[2] Phil. Mag., 15, 1 (1908).

[3] In place of a black body we might consider a partially reflecting one. The equations thus obtained are more complicated, but lead also to the simple equation (7).

receives energy, f the force, and V the velocity of light, we have in rational units the formula,

$$f = \frac{1}{V}\frac{dE}{dt}. \tag{1}$$

This important equation, which was obtained by Maxwell as a consequence of his electromagnetic theory, and by Boltzmann through the direct application of the laws of thermodynamics, has recently been verified with remarkable precision in the beautiful experiments of Nichols and Hull.[1]

A body subjected to the pressure of radiation will acquire momentum, and if we are to accept the law of conservation of momentum we must conclude that some other system is losing in the same direction an equivalent momentum. We are thus led inevitably, as Poynting has shown, to the idea that the beam of radiation carries not only energy, but momentum as well.

The body subject to the constant force of radiation f will obviously acquire momentum at the rate,

$$\frac{dM}{dt} = f. \tag{2}$$

Combining equations (1) and (2) gives,

$$\frac{dE}{dM} = V. \tag{3}$$

The ratio of the acquired energy to the acquired momentum is equal to the velocity of light. The beam of radiation must, therefore, possess energy and momentum in the same ratio. Hence for the beam itself, or any part of it,

$$\frac{E}{M} = V. \tag{4}$$

To any one unfamiliar with the prevailing theories of light, knowing only that light moves with a certain velocity and that in a beam of light momentum and energy are being carried with this same velocity, the natural assumption would be that in such a beam *something possessing mass moves with the velocity of light and therefore has momentum and energy*. Notwithstanding its apparent divergence from the commonly accepted light theories, I propose to adopt this view and see whither it leads.

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[1] Phys. Rev., 17, 26 and 91 (1903).

Postulating the validity of the fundamental conservation laws mentioned above, we shall need in the following development only this one cardinal assumption, that a beam of radiation possesses not only momentum and energy, but also mass, traveling with the velocity of light, and that a body absorbing radiation is acquiring this mass as it also acquires the momentum and the energy of the radiation. Therefore a body which absorbs radiant energy increases in mass.

The amount of this increase is readily found. If in general we write momentum as the product of mass and velocity, then the momentum of any part of a beam of radiation having the mass m will be given by the equation,

$$M = mV. \tag{5}$$

The increase dM in the momentum of the body absorbing the radiation will therefore equal the increase dm in its mass, multiplied by the velocity of light.

$$dM = Vdm. \tag{6}$$

Combining this equation with (3), we find

$$dm = \frac{dE}{V^2}, \tag{7}$$

or if we write $V = 3 \times 10^{10}$ cm. per second,

$$dm = 1.111 \times 10^{-21}\, dE.$$

Thus a body receiving or emitting radiant energy gains or loses mass in proportion, and by the amount 1.111×10^{-21} grams for every erg. This is a small quantity indeed, but one which is not to be neglected.

Assuming the fundamental conservation law, we must regard mass as a real property of a body which depends upon its state and not upon its history. Hence it is obvious that if in any other way than by radiation the body gains or loses energy, it must still gain or lose mass in just the above proportion. In other words, any change in a body's content of energy is accompanied by a definite change in its mass, regardless of the nature of the process which the energy change accompanies.[1]

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[1] I was first led to an investigation of the relation of mass to energy by the work of Landolt on the change of weight in chemical reactions. But it is obvious from equation (7) that although there always will be a loss of mass in a reaction which is accompanied by the evolution of energy, this loss in the case of any ordinary reaction will be far too small to measure. In fact, Landolt has very recently shown (Ber. Berlin. Akad., 1908, 354) that when all possible precautions are taken there is no measurable change of weight in the reactions which he studied.

Since, therefore, when a body loses a given quantity of energy it always loses a definite quantity of mass, we might assume that if it should lose all its energy it would lose all its mass, or, in other words, that the mass of a body is a direct measure of its total energy, according to the equation,

$$m = \frac{E}{V^2} \tag{8}$$

We should then regard mass and energy as different names and different measures of the same quantity, and say that 1 gram equals 9×10^{20} ergs in the same sense that we say that one meter equals 39.37 . . . . inches.

Plausible as this view seems, it rests upon an additional hypothesis besides the fundamental postulate which we have chosen. We shall use, therefore, not equation (8) but equation (7) as the basis of the following work.

It is to be noted that equation (8) has also been obtained by Einstein (*loc. cit.*), who derived it from the general equations of the electromagnetic theory, with the aid of the so-called principle of relativity. That a different method of investigation thus leads to the same simple equation we have here deduced speaks decidedly for the truth of our fundamental postulate.[1]

Comstock (*loc. cit.*), from electromagnetic theory alone, has also concluded that mass is proportional to energy, but his equation is

$$m = \frac{4}{3}\,\frac{E}{V^2}.$$

To investigate, for the cases studied by Comstock, the cause or the justification for this appearance in the equation of the factor $\frac{4}{3}$ would lead too far into electromagnetic theory, from which in the present paper I wish to hold entirely aloof.

Before proceeding to develop fully the consequences of equation (7) it may be well to point out an apparent inconsistency in the equations for the momentum and the energy of a beam of radiation. The momentum of the beam of mass m we have given in equation (5) as

$$M = mV.$$

From our assumption that the energy of the beam is simply the kinetic

[1] Einstein, however, obtains (8) as an approximate formula, while we obtain both (7) and (8) as perfectly exact equations.

energy of the moving mass m, we might expect from our knowledge of elementary mechanics to find for the energy the equation,

$$E = \tfrac{1}{2} m V^2,$$

whereas, in fact, we find from equations (4) and (5) that

$$E = m V^2. \tag{9}$$

We shall see, however, in the next section that this comparison of equations (5) and (9), instead of demolishing our theory, actually furnishes a remarkably satisfactory argument in its favor.

Non-Newtonian Mechanics

One of the interesting branches of modern mathematics has grown out of the study of those geometries which would result from the change of one or more of the axioms of Euclid. These non-Euclidian geometries present the properties of purely imaginary kinds of space, and are therefore so far mere exercises in logic, without any physical significance. But their investigation was doubtless prompted in some cases by the belief that experiment itself may sometimes show that there are deviations from the ordinary laws of space when these laws are subjected to tests of a different order from those of common mensuration. Indeed it is not unlikely that Euclidian geometry may prove inadequate when we are able to subject to an accurate metric investigation the vast stretches of interstellar space or the minute regions which we believe to be encompassed within an atom or an electron.

The science of mechanics, like geometry, has been built up from a set of simple axioms, which were laid down by Newton. But the conclusions of the previous section lead us to modify one of these axioms and thus lay the foundation of a system of non-Newtonian mechanics.

The axiom which we must surrender is the one which states that the mass of a body is independent of its velocity. We have concluded that mass is proportional to content of energy. When a body is set in motion it gains kinetic energy, and therefore its mass must change with its velocity. In place of the axiom which we have abandoned we must substitute equation (7).

Before investigating the consequences of this step it is necessary to define exactly the principal mechanical quantities which we are to use.

Extension in space (l) and time (t) will be measured in the usual way and the centimeter and the second will be employed as units.

Force (f) will be given its usual significance, and the unit, the dyne, will be that force which, acting upon the international standard kilogram when the latter is at rest, imparts to it an initial acceleration of .001 $\frac{\text{cm}}{\text{sec}^2}$.

The momentum (M) of a moving body will be measured by the time in which it is brought to rest under the influence of a constant opposing force of one dyne acting in the line of its motion.

The mass (m) of a moving body will be defined as the momentum divided by the velocity (v), that is,

$$m = \frac{M}{v}. \tag{10}$$

The limiting ratio of the momentum of a body to its velocity, when it is brought to rest, will be called its mass when at rest. The unit of mass is the gram.

The kinetic energy (E') of a body will be measured by the distance through which it will move before being brought to rest by a constant opposing force of one dyne acting in the line of the body's motion. The unit of energy will be the erg.

These definitions, although somewhat unusual in form, are perfectly consistent with the ordinary definitions of Newtonian mechanics. But they have been so chosen as to be consistent also with equation (7) and the fundamental conservation laws. Obviously equation (7) itself is not inconsistent with these conservation laws, for although a body increases in mass as it gains kinetic energy, some other system is losing the same mass as it loses the same energy.

In accordance with the above definitions we may write,

$$dM = fdt. \tag{11}$$

$$dE' = fdl. \tag{12}$$

Let us consider a body, originally moving with a velocity v, subjected for the time dt to a force f in the line of its motion. Its momentum and kinetic energy will change according to (11) and (12) by the amounts,

$$dM = fdt,$$

$$dE' = fdl = fvdt.$$

Hence

$$dE' = vdM. \tag{13}$$

So far the equations are those of Newtonian mechanics, but now in substituting for M from equation (10) we must regard m as a variable, and write,

$$dE' = mvdv + v^2dm. \tag{14}$$

This will be our fundamental equation connecting the kinetic energy of a body with its mass and velocity.

Introducing now the relation of mass to energy given in equation (7), we may write,

$$dE' = V^2dm,$$

and combining this equation with (14) gives,

$$V^2dm = mvdv + v^2dm.$$

This equation, containing only two variables, m and v, and the constant V, may readily be integrated as follows: By a simple transformation,

$$\left(1 - \frac{v^2}{V^2}\right)dm = \frac{mvdv}{V^2}.$$

Writing $\beta = \frac{v}{V}$, and noting that

$$\frac{vdv}{V^2} = -\tfrac{1}{2}d(1 - \beta^2),$$

we see that

$$\frac{dm}{m} = -\tfrac{1}{2}\frac{d(1 - \beta^2)}{1 - \beta^2}.$$

Hence

$$\log m = -\tfrac{1}{2}\log(1 - \beta^2) + \log m_o,$$

where $\log m_o$ is the integration constant. Therefore,

$$\log \frac{m}{m_o} = \log (1 - \beta^2)^{-\frac{1}{2}}, \quad \text{or,}$$

$$\frac{m}{m_o} = \frac{1}{(1 - \beta^2)^{\frac{1}{2}}}. \tag{15}$$

This is the general expression for the mass of a moving body in terms of β, the ratio of its velocity to the velocity of light. When β is zero, $m = m_o$. m_o represents, therefore, the mass of the body at rest.

If we substitute in this equation numerical values of β we find that, while the quotient $\frac{m}{m_o}$ becomes infinite when the velocity equals the velocity of light, it remains almost equal to unity until the velocity of

light is closely approached. Thus a ton weight given the velocity of the fastest cannon ball would, according to this equation, gain in mass by less than one-millionth of a gram. It is obvious that, except in those unusual cases in which we deal with velocities comparable with that of light, our non-Newtonian equations are identical with those of ordinary mechanics far within the limits of error of the most delicate experiments.

Recently, however, it has been possible to study, in the negative particles emitted by radio-active substances, bodies which sometimes move with a velocity only a little less than that of light. In a series of remarkably skillful experiments Kaufmann[1] was able to measure the ratio of electric charge to mass $\left(\frac{e}{m}\right)$ for negative particles moving at different speeds. Assuming that the charge is constant, the fact that $\frac{e}{m}$ varies with the speed of the particle must be attributed to a variation of the mass with the speed. On this assumption it is possible to calculate from Kaufmann's experiments the values of $\frac{m}{m_o}$ at the different velocities.

The mass of a negative particle is usually spoken of as electromagnetic mass, but if we are to hold to our definitions we must recognize only one kind of mass. In general, we have defined the mass of a moving body as the quotient of the time during which it will be brought to rest by unit force, divided by the initial velocity. It matters not what the supposed origin of this mass may be. Equation 15 should, therefore, be directly applicable to the experiments of Kaufmann. In the following table are given the values of $\frac{m}{m_o}$ found for the different observed values of β in the second column. The third column shows those values of β which would correspond with the same values of $\frac{m}{m_o}$ according to equation (15).

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[1] Phys. Zeit., 4, 54 (1902); Ann. Phys., 19, 487 (1906).

$\frac{m}{m_0}$	β (observed).	β (calculated).
1.0	0.0	0.0
1.34	0.73	0.67
1.37	0.75	0.69
1.42	0.78	0.71
1.47	0.80	0.73
1.54	0.83	0.76
1.65	0.86	0.80
1.73	0.88	0.82
2.05	0.93	0.88
2.14	0.95	0.89
2.42	0.96	0.91

It will be seen that the observed values of β follow to a remarkable degree the same trend as those which are calculated by equation (15), but are in every case 6 to 8 per cent. higher.[1] I believe that these differences lie within the limits of experimental error of Kaufmann's measurements. It is true that he claims a higher degree of accuracy, but, notwithstanding the extreme care and delicacy with which the observations were made, it seems almost incredible that measurements of this character, which consisted in the determination of the minute displacement of a somewhat hazy spot on a photographic plate, could have been determined with the precision claimed. Moreover, Planck[2] and Stark[3] have pointed out certain corrections which probably should have been made by Kaufmann and which would produce a material change in his results.[4]

That a charged particle must possess mass in virtue of its charge, and that this mass must vary with the velocity of the particle, was shown to be a consequence of the electromagnetic theory by J. J.

[1] The constancy of the difference between the observed and calculated values of β is striking and would alone indicate some constant error in Kaufmann's results.

[2] Verhandlung Deutsch. Phys. Ges., 9, 301 (1907).

[3] *Ibid.*, 10, 14 (1908).

[4] In reply to Planck, see Kaufmann, *Ibid.*, 9, 667 (1907).

Thomson and by Heaviside, and numerous attempts have been made to find the exact expression for the change of mass with the velocity. But before this can be done some assumption is necessary as to the shape of the particle and the distribution of its charge. The three theories of the simple negative particle or electron which are now most discussed are due to Abraham, Bucherer, and Lorentz.[1] The first assumes that the electron is and remains a rigid sphere; the second assumes an electron which is spherical when at rest, but which in motion contracts in the direction of its translation and expands laterally so as to keep a constant volume; the third assumes an electron similar to the second, which contracts in the direction of translation, but which does not change its other dimensions. On the basis of these theories and from known electromagnetic principles three equations have been obtained for the value of $\frac{m}{m_o}$ as a function of β, namely

$$(a) \quad \frac{m}{m_o} = \tfrac{3}{4} \frac{1}{\beta^2}\left(\frac{1+\beta^2}{2\beta} \log \frac{1+\beta}{1-\beta} - 1\right).$$

$$(b) \quad \frac{m}{m_o} = \frac{1}{(1-\beta^2)^{\frac{1}{2}}}.$$

$$(c) \quad \frac{m}{m_o} = \frac{1}{(1-\beta^2)^{\frac{1}{2}}}.$$

The extraordinary significance of the similarity of the first two of these equations and the identity of the third with equation (15), which we have derived from strikingly different principles, needs no emphasis. Kaufmann shows that his results agree better with the first two of these equations than with the third; but to regard this as serious evidence as to the validity of equation (15) would, as Planck has pointed out, be laying too great a stress on the accuracy of the experimental observations.

The agreement of Kaufmann's results with the above equations has led him, and all others who have discussed his results, to the conclusion that all of the mass of an electron is electromagnetic.

Their argument is based on the assumption that ordinary mass — the mass of "ponderable matter" — is independent of the velocity, while "electromagnetic mass" varies with the velocity according to one of

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[1] For a discussion of these theories, see Abraham, Theorie der Elektricität, 2, Leipzig, 1905; and Bucherer, Mathematische Einführung in die Elektrontheorie, Leipzig, 1904.

the above equations. But in this paper we have assumed that all mass is one, and that any bodies, whether charged or not, moving at the velocities of Kaufmann's electrons would show the same values of $\frac{m}{m_o}$.

There is some hope that the correctness of this view may be decided by an experimental study of the mass of a positive or α particle at different speeds. According to the ordinary view the mass of such a positive particle as issues from a radio-active source is chiefly that of its "ponderable" matter and only to a very small extent "electromagnetic mass." It would, therefore, be generally assumed that at the highest velocity of the particle, about one-tenth of the velocity of light, it would have substantially the same mass as at rest. According to our view, on the other hand, the mass of this or any other particle would change with the velocity in the same way as the mass of an electron. From equation (15) we should, therefore, expect the particle moving with one-tenth of the velocity of light to have a mass 2 per cent. greater than when at rest. The experimental difficulties in testing this point would be very great, of course, but perhaps not insurmountable.

The plausibility of our fundamental assumption which led directly to equation (15) has been greatly increased by the agreement between this equation and Kaufmann's results, and also perhaps by the similarity between this equation and those deduced from electromagnetic theory. But the simplest as well as the strongest evidence of the correctness of our point of view comes from a consideration of the non-Newtonian equation for kinetic energy.

The integration of equation (14) obviously does not yield the simple Newtonian equation,

$$E' = \tfrac{1}{2}\, mv^2.$$

This equation must be replaced by one that is obtained as follows:

Let a body, which at rest has the mass m_o, be given the velocity v. As its energy changes, its mass will change according to equation (7), and

$$m - m_o = \frac{E'}{V^2};$$

where E' is the acquired kinetic energy and $m - m_o$ is the increase in mass. Eliminating m_o between this equation and (15) gives

$$E' = m V^2 [1 - (1 - \beta^2)^{\frac{1}{2}}]. \qquad (16)$$

This is the general formula for the kinetic energy of a moving body.

As usual, β represents $\frac{v}{V}$, the ratio of the velocity to the velocity of light.

From equations (10), (15), and (16) may be constructed the whole science of non-Newtonian dynamics, of which Newtonian dynamics furnishes a limiting case, namely, for velocities which are negligible in comparison with the velocity of light.

For example, expanding (16) by the binomial theorem gives

$$E' = m V^2(\tfrac{1}{2}\beta^2 + \tfrac{1}{8}\beta^4 \ldots). \tag{17}$$

For low values of β the higher terms may be neglected and

$$E' = \tfrac{1}{2} m v^2.$$

That is, the limit approached by the kinetic energy of a body as the velocity approaches zero is, as in ordinary mechanics, one-half the product of the mass and the square of the velocity. At the other limit of velocity when $\beta = 1$ it follows from (16) that

$$E' = m V^2. \tag{18}$$

Between these two limits it is obvious that

$$\tfrac{1}{2} m v^2 < E' < m v^2.$$

The momentum and the kinetic energy of any mass moving with the velocity of light are, therefore,

$$M = m V,$$
$$E' = m V^2;$$

but these equations are identical with (5) and (9), which we obtained for the momentum and the energy of a *beam of light.*

Further Consequences of the Theory

The view here proposed, which appears at first sight a reversion to the old corpuscular theory of light, must seem to many incompatible with the electromagnetic theory. If it were really so I should not have ventured to advance it, for the ideas announced by Maxwell constitute what may no longer be regarded as a theory, but rather a body of experimental fact. The new theory is offered, not in any sense to replace, but to supplement the accepted theories of light. I hope in another paper to show that it is entirely consistent with those theories.

Such a proof may constitute a step towards one of the obvious goals of present day science, the complete mechanical explanation of electromagnetic phenomena, or, what is very nearly the same thing, an electromagnetic explanation of the phenomena of ordinary mechanics. In the meantime a few of the more salient conclusions of our theory may be cursorily examined.

In the first place, it should be noticed that, while the theory is consistent with a modified corpuscular theory of light, it does not necessarily imply that light is corpuscular. The stream of mass issuing from a radiating body may be made up of discrete particles or it may be continuous. In the absence of any evidence on this point we may assume the latter. Whatever it may be that is emitted, it is not matter in the ordinary sense, as is to be seen from the following considerations.

According to equation (15), any body of finite mass increases in mass as it increases in velocity, and would possess infinite mass if it could be given the velocity of light. *Therefore that which in a beam of light has mass, momentum, and energy, and is traveling with the velocity of light, would have no energy, momentum, or mass if it were at rest, or, indeed, if it were moving with a velocity even by the smallest fraction less than that of light.* After this extraordinary conclusion it would at present be idle to discuss whether the same substance or thing which carries the radiation from the emitting body continues to carry it through space, or, indeed, whether there is any substance or thing connected with the process.

If we assume an ether pervading space and assume that this ether possesses no mass except when it moves with the velocity of light, it is obvious that an ether drift could in no way affect a beam of radiation nor be detected by any mechanical means. If we are to assume such an ether we may as well assume it to be at rest.

The question whether a method is conceivable by which absolute motion in space may be distinguished from relative motion must be answered definitely in the affirmative by one who accepts the above equations of non-Newtonian mechanics. A body is absolutely at rest when any motion imparted to it increases its mass, or when a certain force will give it the same acceleration in any direction. It is true that metaphysicians hold that in the strictest sense absolute motion is not only unknowable, but unthinkable; but we may say at least that the above method permits theoretically the detection of absolute trans-

lational motion in the same sense that a study of centrifugal forces enables us to detect absolute rotational motion.

Summary

It is postulated that the energy and momentum of a beam of radiation are due to a *mass* moving with the velocity of light.

From this postulate alone it is shown that the mass of a body depends upon its energy content. It is therefore necessary to replace that axiom of Newtonian mechanics according to which the mass of a body is independent of its velocity, by one which makes the mass increase with the kinetic energy.

Retaining all the other axioms of Newtonian mechanics and assuming the conservation laws of mass, energy, and momentum, a new system of mechanics is constructed.

In this system momentum is mv, kinetic energy varies between $\frac{1}{2}mv^2$ at low velocity and mv^2 at the velocity of light, while the mass of a body is a function of the velocity and becomes infinite at the velocity of light. The equation obtained agrees with the experiments of Kaufmann on the relation between the mass of an electron and its velocity. It is, moreover, strikingly similar to the equations that have been obtained for electromagnetic mass.

The new view leads to an unusual conception of the nature of light. It offers theoretically a method of distinguishing between absolute and relative motion.

Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology,
May 14, 1908.

PROCEEDINGS OF THE SOCIETY OF ARTS

FORTY-SIXTH YEAR, 1907-1908

BOSTON, February 13, 1908.

THE 645th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, February 13, at eight o'clock, about one hundred and sixty persons being present. Dr. Robert P. Bigelow presided.

Mr. F. W. McCarter was elected to membership.

The chairman introduced Professor Thomas A. Jaggar, Jr., of the Institute of Technology, who spoke on "The Evolution of Bogoslof, a New Volcano in Behring Sea." Professor Jaggar's address was illustrated by a large number of lantern slides, many of which were taken by his party during a recent excursion to the Behring Sea. He gave a most interesting account of the volcanic origin of this island in the Behring Sea, and his slides clearly showed the island of Bogoslof in its several different conditions since it first rose from the sea. The thanks of the Society were extended to the speaker by the chairman, and the meeting adjourned at 9.30.

BOSTON, February 27, 1908.

The 646th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, February 27, at eight o'clock, about one hundred and thirty persons being present. Colonel Edmund H. Hewins presided.

The chairman introduced Mr. Charles B. Burleigh, of the General Electric Company, Boston, who discussed in a most interesting manner the essential features of steam turbines generally, and of the Curtis turbine in particular. Mr. Burleigh held the attention of the audience until 9.30, showing nearly one hundred lantern slides. After the address

an interesting discussion followed, and many questions were asked. The chairman extended the thanks of the Society to the speaker. The meeting adjourned at 10.15.

BOSTON, March 12, 1908.

The 647th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, March 12, at eight o'clock, about one hundred persons being present. Dr. Robert P. Bigelow presided.

The chairman introduced Mr. Gorham Dana, Manager of the Underwriters' Bureau of New England, who gave a most interesting talk on "Recent Developments in Fire Protection Devices."[1] The lecture was illustrated by a large number of specimens and some excellent lantern slides. The chairman extended the thanks of the Society to the speaker, and the meeting adjourned at 9.45.

BOSTON, March 26, 1908.

The 648th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, March 26, at eight o'clock, about two hundred and thirty persons being present. Professor Charles R. Cross presided.

The chairman then introduced Mr. J. E. Brulatour, of the Lumière Company, who spoke on "The Lumière Autochrome Plates." Mr. Brulatour showed numerous slides made on these plates and explained the process of the three-color photography. He had but little to say, allowing the slides to speak for themselves. A large number of most interesting slides were shown and many questions were asked of Mr. Brulatour at the close of the address. He also showed a large number of color plates, too large for insertion in the lantern. The thanks of the Society were extended to the speaker by the chairman, and the meeting adjourned at 9.30.

BOSTON, April 9, 1908.

The 649th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, April 9, at eight

[1] Printed above, pp. 141–163.

o'clock, about sixty persons being present. Professor R. H. Richards presided.

The chairman introduced Mr. E. G. Acheson, President of the Acheson International Graphite Company, of Niagara Falls, who spoke on "The Deflocculation of Nonmetallic Amorphous Bodies, with Special Reference to Graphite as a Lubricant." Mr. Acheson's talk was illustrated by numerous experiments, clearly showing the means by which his deflocculated, or finely divided, graphite could be permanently suspended in water by the addition of a small amount of vegetable matter, and how readily acids or other impurities caused its precipitation. As a lubricant it can be suspended in either water or oil, and has produced remarkable results both as a cylinder oil and as an ordinary spindle lubricant. It has even been suggested that lubricating projectiles used in our large guns will greatly prolong the life of the rifle, which ordinarily is good for less than one hundred shots. The intense friction of the projectile at the high velocities attained quickly destroys the gun. The graphite would largely reduce this friction and increase the muzzle velocity. The Society extended a vote of thanks to the speaker, and the meeting adjourned at 9.30.

BOSTON, April 23, 1908.

The 650th regular meeting of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, April 23, at eight o'clock. Colonel Edmund H. Hewins presided.

The chairman introduced Professor Dugald C. Jackson, Head of the Department of Electrical Engineering, Institute of Technology, who spoke on "Factors Governing the Rates of Public Service Corporations and the Government Control of Rates." The lecture was of timely interest and will appear in the next issue of the TECHNOLOGY QUARTERLY. The meeting adjourned at 9.30.

BOSTON, May 21, 1908.

The 651st regular meeting and the 46th ANNUAL MEETING of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, May 21, at eight o'clock, about one hundred and ten persons being present. Dr. A. A. Noyes presided.

The minutes of the last meeting were read by the Secretary and approved.

The report of the Executive Committee was presented by the Secretary for the Executive Committee.

REPORT OF THE EXECUTIVE COMMITTEE OF THE SOCIETY OF ARTS

The report of the Executive Committee of the SOCIETY OF ARTS of a year ago entered somewhat at length into the purposes of the Society and its relation to the Institute and the public.

That the Society has not for a series of years fulfilled its purposed function has been only too manifest, and this condition of affairs has been an anxiety to those charged with the conduct of its affairs.

The absence of a permanent President would seem to have contributed to the delay in formulating an active and persistent policy, but it is hoped during the coming year some systematic effort may be made to enable the Society to take its proper place in this community.

It is hoped that the Committee of the Corporation on the SOCIETY OF ARTS may join with your Executive Committee to this end.

During the year twenty-one (21) members have been dropped for nonpayment of dues, nine (9) have resigned, chiefly as the result of persistent efforts to collect dues in arrears, one (1) has died, and two (2) have been elected to membership. There are at present two hundred and ninety-four (294) associate members, forty-six (46) of whom have paid twenty (20) or more annual assessments and are entitled to the benefits of life membership without further payment of dues.

The attendance at the meetings has been fairly good. Eighteen (18) has been the smallest, and two hundred and twenty (220) the largest audience, with fifty (50) or sixty (60) a fair average.

There have been thirteen (13) meetings this winter, with talks on the following topics:

"Chilled Car Wheels," by Mr. F. A. Beebee, Assistant Manager of the Griffin Wheel Company, Chicago.

"Physical History of the Grand Cañon District," by Professor D. W. Johnson, of Harvard University.

"Refrigeration," by Mr. Norman H. Cheney, Chief Engineer of the Merchants' Cold Storage and Freezing Company, Providence, Rhode Island.

"Forestry," by Mr. Philip W. Ayers, State Forester of New Hampshire.

"Denatured, or Industrial, Alcohol," by Rufus F. Herrick, Chemist, of Boston.

"Ascents of Orizaba and Colima, Two Mexican Volcanoes," by Professor John E. Wolff, of Harvard University.

"The Evolution of Bogoslof, a New Volcano in Behring Sea," by Professor Thomas A. Jaggar, Jr., Institute of Technology.

"The Curtis Steam Turbine," by Mr. Charles B. Burleigh, of the General Electric Company, Boston.

"Recent Developments in Fire Protection Devices," by Mr. Gorham Dana, of Boston.

"The Lumière Autochrome Plates," by Mr. J. E. Brulatour, of the Lumière Company, New York.

"The Deflocculation of Nonmetallic Amorphous Bodies, with Special Reference to Graphite as a Lubricant," by Mr. E. G. Acheson, President of the Acheson International Graphite Company of Niagara Falls.

"Factors Governing the Rates of Public Service Corporations and the Government Control of Rates," by Professor D. C. Jackson, Institute of Technology.

"The Quebec Bridge Disaster," by Professor George F. Swain, Institute of Technology.

Your Committee earnestly desires any suggestions as to methods by which the work of the Society may be made of benefit to the community and to the Institute of Technology.

The report was accepted.

Mr. I. K. Litchfield was duly elected to associate membership.

W. S. Leland was elected Secretary, and the following members of the Executive Committee for the year 1908–09: Colonel Edmund H. Hewins, Mr. W. S. Johnson, Mr. I. K. Litchfield, Professor W. H. Walker, Dr. C. J. H. Woodbury.

There being no further business to be presented at the meeting, the chairman introduced Professor George F. Swain, Head of the Civil Engineering Department, Institute of Technology, who spoke on "The Quebec Bridge Disaster." Professor Swain explained the different forms of bridge construction, and showed the fundamental principles which are required in a safe design. He showed a large number of slides of substantial and typical bridges, and then showed slides showing the detail and general construction of the Quebec Bridge. He clearly explained the reason of collapse, and how the lattice work which failed

in this bridge compared in relative size and strength to the lattice work on other bridges which have proved satisfactory for a number of years. The lecture was most interesting and instructive, and the chairman extended the thanks of the Society to the speaker. The meeting adjourned at 9.30.

WALTER S. LELAND, *Secretary.*

BOOK REVIEWS

STANDARD HANDBOOK FOR ELECTRICAL ENGINEERS[1]

IT is impossible within the limits of a review to give any detailed comment on the contents of a comprehensive handbook such as the new "Standard Handbook for Electrical Engineers." The value of the material is largely affected by its availability, and in this case the general arrangement is good and the index seems to be very complete. The inclusion of certain general tables omitted from some similar handbooks is a distinct advantage. The diagrams are the least satisfactory feature of the book, as many of them are too much reduced in size or too crowded to be quickly intelligible, and others are lacking in the sharpness which might reasonably be expected. The rapidity with which the first edition of this book is being exhausted is a conclusive proof that it meets a widespread demand. C. H. P.

MINING AND METALLURGY IN SOUTH AFRICA[2]

THE bound volume of the Proceedings of the Chemical, Metallurgical, and Mining Society of South Africa is always a welcome addition to the literature of mining and metallurgy. Volume IV, covering the period of July, 1903, to June, 1904, was published in Johannesburg early this year.

Among the papers which are printed, with complete discussion on each, we find two or three papers on Hygiene of Mining, including the Relation of Mine Gases to Tuberculosis, Ventilation of Deep Levels, and Ankylostomiasis, and another which may perhaps be classed with these, on the Composition of Tobacco Smoke.

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[1] Standard Handbook for Electrical Engineers. New York: McGraw, 1908. 20 + 1,283 pp., il., 16mo. $4.00.

[2] Chemical, Metallurgical, and Mining Society of South Africa. Proceedings, Vol. IV, 1903–04, with Appendix. Johannesburg, Transvaal. Published by the Society, 1908.

There are two papers on Rock Crushing, considered with reference to the wet and the dry process, respectively; and a paper on Slime Treatment. The Cyanide Process naturally receives a large portion of the attention of the Society, the present volume containing no less than eight papers on various aspects of this process.

The Manufacture of Explosives, Hauling and Transportation of Ore, Smelting and Cupellation, and the Flow of Water also receive attention in this volume.

The appendices contain Minutes of the Proceedings of the Society, Report of the Committee on Cyanide Poisoning, Contributions and Correspondence, Obituary Notices, and Notices and Abstracts of Articles and Papers, classed under Chemistry, Metallurgy, Mining, and Miscellaneous.

The volume closes with Index of Authors and Subjects.

PUBLICATIONS[1]

ARCHITECTURE

Truman H. Bartlett.—Essay on the Portraits of Lincoln, in Carl Schurz's Biographical Essay on Abraham Lincoln. Boston: Houghton, Mifflin & Co. December, 1907. pp. 134. 18 il. 4to.

Contains Carl Schurz's brief biography of Lincoln; essay on the portraits of Lincoln by T. H. Bartlett, illustrated by 18 photogravure prints of portraits, life mask, and hands of Lincoln; sonnet on the mask of Lincoln by R. W. Gilder; poem on the hand of Lincoln by E. L. Stedman.

The book follows, in general form, the recent editions of the Life of Cardinal Woolsey and the Autobiography of Benjamin Franklin, published by Houghton, Mifflin & Co.

BIOLOGY

S. C. Prescott and *C.-E. A. Winslow.*—Elements of Water Bacteriology, with Special Reference to Sanitary Water Analysis. Edition 2. New York: John Wiley & Sons. 1908.* pp. 12 + 258. 1 il. 12mo.

S. C. Prescott and *C.-E. A. Winslow.*—The Relative Value of Dextrose Broth, Phenol Broth, and Lactose Bile as Enrichment-Media for the Isolation of Bacillus coli. *American Journal of Public Hygiene,* Vol. 18, pp. 19–26. February, 1908.

Burt R. Rickards.—(1) Sputum Shaking and Sedimenting Apparatus. (2) A Rabies Collecting Outfit. *Journal of Infectious Diseases,* pp. 119–122. il. May, 1907.*

Burt R. Rickards.—Diphtheria, Sewer Gas, and Infection. Editorial in *American Journal of Public Hygiene,* Vol. 17, pp. 262–267. August, 1907.*

Burt R. Rickards and *H. W. Hill.*—Milk Commissions of the United

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[1] In order that the extent of productive work carried on at the Institute may be better known, it is proposed to publish quarterly a list of the publications of officers of the Institute, together with abstracts when possible. In this list the publications are arranged alphabetically by departments and then alphabetically by authors.

The asterisk after the title indicates that a copy of the publication has been placed in the library of the Institute.

States—A Synopsis of Their Work. Editorial in *American Journal of Public Hygiene*, Vol. 17. May, 1907.*

Chemistry and Chemical Engineering

F. J. Moore and *R. D. Gale.*—The Colored Salts of Schiff's Bases—(1) The Hydrochlorides of Bases Formed by Condensing p-Amino Dimethylaniline with Aromatic Aldehydes. *Journal of the American Chemical Society*, pp. 394–403, Vol. 30. March, 1908.* (Reprinted, *ante*, p. 200.)

Ellwood B. Spear.—Catalytic Decomposition of Hydrogen Peroxide under High Pressures of Oxygen. *Journal of American Chemical Society*, pp. 195–208. il. Vol. 30. February, 1908.

The article is a condensed translation of a dissertation, Heidelberg, 1907.

The chief results are:

A method has been worked out and an apparatus designed whereby rates of reaction may be measured under high gas pressures.

It has been experimentally determined that the catalytic decomposition of hydrogen peroxide by colloidal solutions of platinum, palladium, iridium, gold, and silver is inappreciably affected by increasing the pressure of the oxygen gas above the reaction-mixture from 1 to 200 atmospheres.

A. A. Noyes, W. C. Bray, and *E. B. Spear.*—Contributions from the Research Laboratory of Physical Chemistry, No. 23: A System of Qualitative Analysis for the Common Elements. Part III. Analysis of the Aluminum and Iron Groups. *Technology Quarterly*, Vol. 21, No. 1. pp. 14–125. March, 1908.*

Edward W. Washburn.—The Theory and Practice of the Iodometric Determination of Arsenious Acid. *Journal American Chemical Society*, Vol. 39, pp. 31–45. il. January, 1908.*

From a consideration of the equilibria involved in a solution containing iodine and arsenious acid, it is shown that in order that the reaction

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^-$$

shall proceed quantitatively toward the right, it is necessary that the concentration of hydrogen-ion in the solution at the completion of the titration shall be close to 10^{-7} molal. It is shown that mixtures of sodium bicarbonate and carbonic acid, borax and boric acid, or disodium phosphate and phosphoric acid in the proper proportions will automatically maintain the concentration of hydrogen-ion at the desired value. Identical results are obtained with each of these mixtures, but the phosphate mixture is to be preferred, owing to the non-volatility of the

acid. When the proper conditions are fulfilled, it is shown that the titration of arsenious acid with standard iodine solution can be made with an accuracy of 0.002 per cent., and that the end point is exceedingly delicate and absolutely permanent. Directions are given for preparing the standard solutions and carrying out the titration in order to attain the above mentioned accuracy.

Civil Engineering

C. B. Breed.—Abolition of Grade Crossings at Worcester, Mass. *Railroad Gazette,* Vol. 14, No. 11, pp. 358–461. il. March 13, 1908.

G. A. Goodenough and *L. E. Moore.*—The Strength of Chain Links. *University of Illinois Publications, Bulletin Engineering Experiment Station.* Vol. 5, No. 1, pp. 73. il. September 2, 1907.

George E. Russell.—Notes on Hydraulics. Boston, December, 1907. pp. 80. il.

Drawing

C. W. Sawyer.—Vacation on a Way-Back Farm. *Forest and Stream.* February 25, 1899.

C. W. Sawyer.—Three Rifles and a Shotgun. *Forest and Stream.* August 10, 1901. il.

C. W. Sawyer.—Experimenting with a Ballard. *Shooting and Fishing.* January 1, 1901.

C. W. Sawyer.—Twenty-two Calibre Experimenting and Notes. *Shooting and Fishing.* October 17 and 24, 1901.

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The results of our investigation may be summarized as follows:

1. The density of fused sodium, potassium, lithium and silver nitrate, and silver chlorate, together with mixtures of sodium and potassium nitrate and of lithium nitrate and silver chlorate, had been determined to 0.1 per cent. over a wide range of temperature. In all cases the density was found to be a linear function of the temperature to within a tenth of 1 per cent. Tables giving the specific and molecular volume of the above salts for every ten degrees have been computed.

2. The specific volume of mixtures of sodium and potassium nitrate containing 8 and 2, 5 and 5, and 2 and 8 mols of these salts, respectively, is greater than that computed from the specific volumes of the components, *i. e.*, the solution of one salt in another is accompanied by an expansion. The magnitude of this expansion is small, being a maximum (0.5 per cent.) for equimolecular mixtures.

In the case of an equimolecular mixture of lithium nitrate and silver chlorate, on the other hand, a contraction of 20 per cent. occurs.

3. The specific conductance of the same salts and salt mixtures has been determined over the same temperature interval as the density. The results show that, except in the case of lithium nitrate and silver chlorate, which could be measured over only a limited range of temperature on account of their instability, the specific conductance is not strictly proportional to the temperature, but increases less and less rapidly as the temperature rises. For the limited range of temperature over which lithium nitrate, silver chlorate, and their mixtures were studied the specific conductance is proportional to the temperature. Tables have been computed giving the specific and equivalent conductance of each salt and mixture for every ten degrees, as well as the temperature coefficient for each interval. The temperature coefficient is, generally speaking, less than one-fifth as great as that for the corresponding aqueous solutions.

4. A study of the computed values of the equivalent conductance shows that this quantity increases very nearly linearly with the temperature. The temperature coefficient decreases, therefore, with increasing temperature, but at any given temperature is slightly greater than that of the specific conductance at the same temperature.

5. The equivalent conductance of the mixtures of the sodium and potassium nitrate is less than that computed from the equivalent conductance of the components. This is most marked in the case of the equimolecular mixture where the difference reaches 3 per cent., an amount considerably greater than can be accounted for by experimental error. It tends to confirm the view that the effect of dissolving one nitrate in another is to decrease the dissociation. Our results do not confirm the conclusion drawn by Poincaré from similar experiments on the conductivity of mixed nitrates, namely, that the conductance of a mixture can be accurately calculated from that of the components by the mixture formula.

6. In the case of an equimolecular mixture of lithium nitrate and silver chlorate, the deviations between observed and computed values of the equivalent conductance are as much as 12 per cent., the computed values being, as before, the larger, indicating a metathesis between the components with corresponding change (decrease) of ionization. This mixture also showed a contraction in volume of 16 per cent.

7. The fluidity, or reciprocal of the absolute viscosity coefficient, of the same series of fused salts was measured over the temperature interval in which their conductivity and density were studied.

In all cases the fluidity was found to be directly proportional to the temperature. Its temperature coefficient is in every case greater than the corresponding temperature coefficient of specific conductance.

8. The ratio

$$\frac{\text{specific conductance}}{\text{fluidity}} = \frac{\kappa}{F},$$

computed for every ten degrees was found to decrease regularly, without exception, with increasing temperature. Foussereau's law of the proportionality between these quantities is, therefore, not confirmed. Our results are, however, in excellent agreement, so far as comparison is possible, with those of Lorenz and Kalmus.

9. The value of

$$f = \frac{\text{fluidity}}{\text{molecular volume}} = \frac{F}{\phi},$$

which we have called molal fluidity, and its temperature coefficient for each ten degrees were also computed. The results show that the molal fluidity is directly proportional to the temperature. The ratio

$$\frac{\text{molal conductance}}{\text{molal fluidity}} = \frac{\Lambda}{f}$$

has also been calculated for every ten degrees. This ratio is practically a constant for potassium nitrate and mixtures of potassium and sodium nitrate over a range of temperature of more than 100 degrees. In the case of sodium, lithium, and silver nitrates the proportionality does not hold quite as rigidly; the ratio decreases with increasing temperature by a small percentage, an amount, however, which we believe cannot be attributed wholly to experimental error. The ratio is approximately a constant for the group of nitrates investigated.

From this it appears, if proportionality between mobility of ions and fluidity be assumed, that increasing the temperature of the fused salts investigated has little effect on their ionization; its tendency is to decrease rather than increase their electrolytic dissociation—a result analogous to the effect on salts in aqueous solutions raised to high temperatures under pressure, as recently shown by Noyes. As this is characteristic of very highly dissociated substances, our results lend weight to the view that a high rather than a low degree of ionization obtains in fused electrolytes.

10. The molal fluidity of mixtures of sodium and potassium nitrate is greater than that computed from the components of the mixture. The difference is nearly constant for a given mixture, *i. e.*, independent of the temperature; it is greatest for equimolecular mixtures. As the equivalent conductance of these same mixtures was found to be less than the calculated values, we have additional evidence that the effect of increased fluidity on the migration velocity of the ions is probably more than neutralized by a diminished dissociation of the mixed salts.

11. The results of this investigation provide a more fundamental experimental basis for the further development of the theory of conduction in fused salts than has hitherto been possible. Although the accumulation of these data is laborious, as it involves three independent investigations on density, conductivity, and viscosity, all of which are of more than ordinary difficulty if a precision better than

1 per cent. is desired, it is to be hoped that other contributions to this important and interesting field of electro-chemistry will be made in the near future.

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CONTRIBUTION FROM THE
SANITARY RESEARCH LABORATORY AND SEWAGE EXPERIMENT STATION
OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

AN INVESTIGATION OF THE SANITARY CONDITION OF THE GOWANUS CANAL, BROOKLYN, NEW YORK

BY CHARLES F. BREITZKE

INTRODUCTION

THE following is an abstract of a part of the thesis submitted in May, 1906, by Norman P. Gerhard and the writer, at that time candidates for the Degree of Bachelor of Science at the Massachusetts Institute of Technology.

The object in view in the preparation of the original thesis on file in the Engineering Library at the Institute was to investigate the condition of the Gowanus Canal, Brooklyn, New York, and to suggest a plan for remedying the nuisance. The sanitary investigation was made by the writer. The discussion of the methods which might be applied to remedy the conditions was written by N. P. Gerhard. In view of the fact that the problem has also been considered by the Brooklyn engineers and that a flushing tunnel is now under construction, it was thought best in the publication of this abstract to omit N. P. Gerhard's part of this study.

FIG. 1.— MAP OF A PORTION OF NEW YORK HARBOR SHOWING THE LOCATION OF THE GOWANUS CANAL

GENERAL DESCRIPTION

Location. — The Gowanus Canal is located in the western part of the Borough of Brooklyn, City of New York, midway between Prospect

Park and Upper New York Bay. The canal is closed at its upper end and opens at the lower end into Gowanus Bay, a part of New York Harbor. Its position is best seen by a study of the appended United States Geological Survey map (Fig. 1).

Construction and Data. — Originally this portion of Brooklyn contained a stream known as Gowanus Creek. Its shores were everywhere surrounded by great salt marshes formed by the combined action of the tide and the wash from the surrounding upland. This inlet was then navigable at all stages of the tide. Since that time the marshes have been entirely filled in, mainly from gravel knolls which were cut

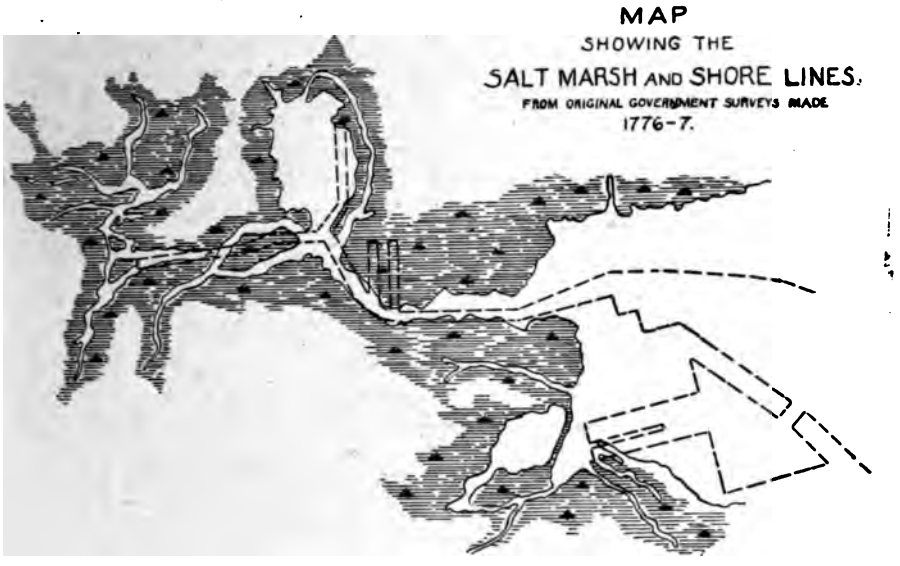
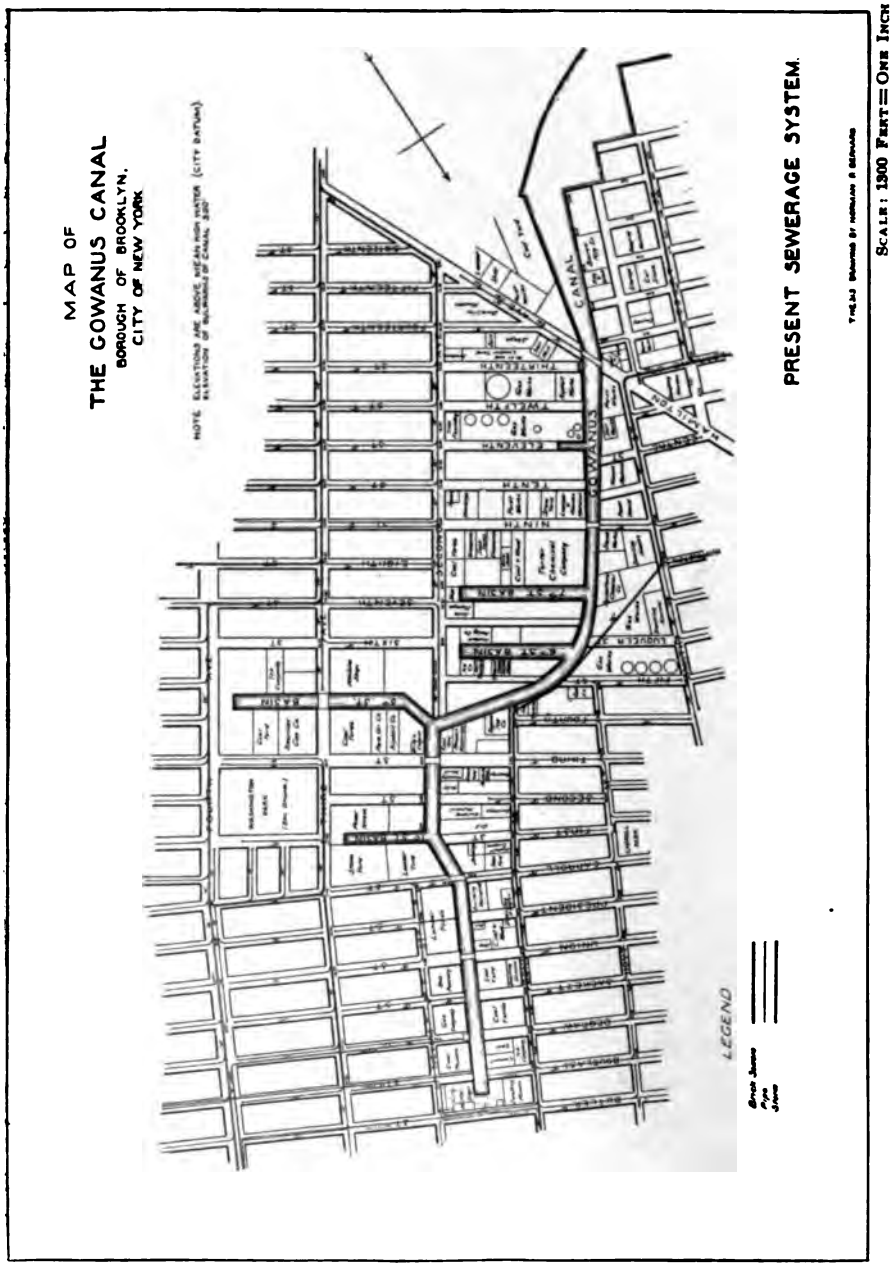


FIG. 2.

down in the western part of the city. The original shore line in 1776 and the present outline of the canal are shown on the accompanying map (Fig. 2). A glance at the topographical map shows that the land slopes down towards the canal on the north, east, and west; while on the south it is flat, this being made land. For the length of a block on either side of the canal the ground is practically level.

The act authorizing the construction of the canal was passed in 1849. The original cost of construction was $452,131, and this was assessed on the portion of the city benefited. The lateral basins provided for were to be built by private enterprise. The date of completion was about 1860.


MAP OF
THE GOWANUS CANAL
BOROUGH OF BROOKLYN,
CITY OF NEW YORK
PRESENT SEWERAGE SYSTEM.
SCALE: 1200 FEET = ONE INCH
LEGEND
GOWANUS
CANAL

The canal (Fig. 3) was constructed with two objects in view. One was to drain this section of the city, including an area of about 1,700 acres, chiefly marshes, and to make it fit for agricultural use and building purposes. The other object was to make a navigable waterway for all river and coasting craft, such as sloops and schooners of light draft, towboats, and barges.

The length of the main canal is about 6,575 feet, and the lateral basins are approximately 3,600 feet in length. The total length is, therefore, about 10,175 feet, or somewhat less than two miles. The legal width of the canal is 100 feet. Its average depth is 10 feet below mean low water, but the variations in depth are considerable. At the head it is about 5 feet deep and it grows gradually deeper as Hamilton Avenue is approached. The total capacity of the canal at mean low water is approximately 10,000,000 cubic feet.

Nature of the Locality. — The locality is chiefly a commercial one and consists largely of factories and yards. Certain portions toward the lower end and on the eastern side are not yet built up, and there remain numerous empty lots. The factories and yards extend the entire length of the canal and for the distance of a block on either side. These include gas works, factories, chemical works, ice plants, salt works, oil refineries, asphalt and paving material plants, building material yards, coal and wood yards, power houses, machine shops and foundries, storage warehouses, junk yards, and city dumps.

Immediately adjoining this business section on either side of the canal is a thickly populated tenement district. Gradually, as the distance from the canal increases, more and more houses are found, and the better residence sections are within five blocks on either side.

The photographs accompanying this article (Figs. 4 to 7) give a general idea of the nature of the locality.

Value of the Property. — The assessed value of the land fronting the canal is $3,315,000. The canal enables the abutters easily to obtain supplies of coal, brick, lumber, oil, etc., from schooners and canal boats towed up the canal by tugs. An examination of records on the amount of traffic on the Gowanus Canal showed that during a recent year 26,680 vessels passed Hamilton Avenue, an average of eighty-seven per day. At Ninth Street, Third Street, and Union Street, the average per day was eighty, forty-eight, and twenty-four vessels, respectively. There is no railroad in this part of the city, and the canal is therefore a great convenience.

FIG. 4.—FIFTH STREET LATERAL BASIN

FIG. 5.—CARROLL STREET BRIDGE

FIG. 6.—VIEW LOOKING SOUTH FROM UNION STREET BRIDGE

FIG. 7.—VIEW LOOKING NORTH FROM CARROLL STREET BRIDGE

Tributary Sewers. — With the single exception of Chicago, Brooklyn was the first city in this country to undertake a complete system of sewerage. Therefore when the sewerage system was planned the designing engineer was dependent upon English experience for data in regard to the amount of sewage to be provided for, as well as for the amount of rainfall from any given storm which reaches a sewer within a given time.

The sizes of sewers were determined mainly by the extremes of rainfall, the household sewage being a very small item in comparison. The sewerage was installed in the early sixties. Brooklyn grew very

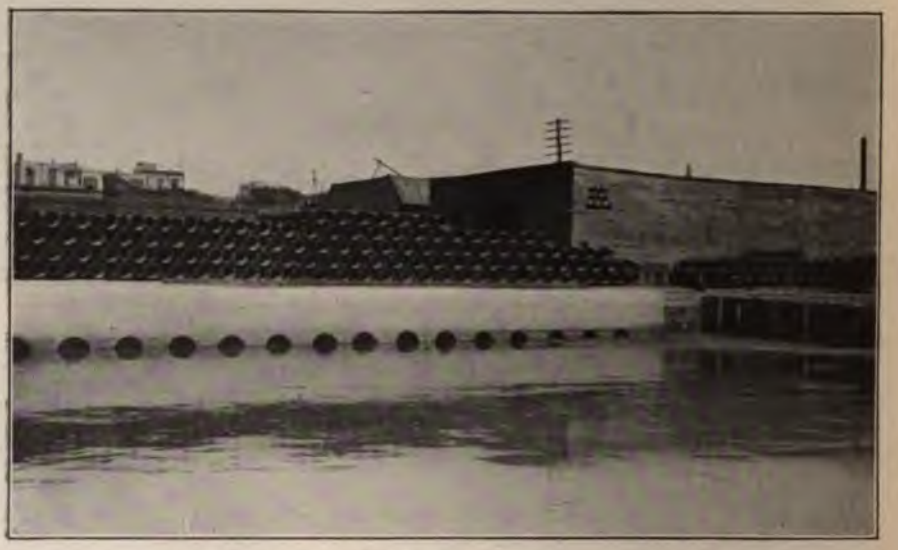


FIG. 8.— OUTLET OF SILT BASIN AT HEAD OF CANAL

rapidly. Consequently by 1888 the sewers became too small, and the legislature of that year passed an act permitting the discharge of storm water sewers into the Gowanus Canal. In 1892 a 15-foot main relief sewer, which intercepts all the storm water in the mains draining that portion of Brooklyn lying south of Greene Avenue, was brought down to the head of the Gowanus Canal, at Butler Street (Fig. 8), and completed. Nothing but storm water was intended to enter this relief sewer, but, whether by accident or design, it is now flowing during dry weather and is discharging sewage into the canal.

In addition, the following storm overflows have also been con-

structed: 78-inch overflow from Nevins Street at the head of the canal; 60-inch overflow from Bond Street at the head of the canal; 42-inch storm sewer on Douglass Street; 90-inch storm sewer on Degraw Street discharging through a silt basin; 78-inch overflow from Third Avenue main sewer discharging at Second Avenue; 72-inch overflow from Bond Street main sewer discharging at foot of Bond Street.

All of these sewers bring down more or less diluted sewage and street washings during times of storm. The contents of the canal are of the vilest sort. Practically all the industrial plants on the streets adjoining the canal discharge directly into it. The following sanitary sewers empty into the canal: 18-inch sewer on Sackett Street; 18-inch sewer on President Street; 12-inch sewer on Carroll Street; 12-inch sewer on Ninth Street; 12-inch sewer on Hamilton Avenue; 48-inch sewer on Grinnell Street.

With the above exceptions, the streets which terminate at the canal have been left unsewered. The reason given is that there was not sufficient grade to drain the sewers into the mains in the streets running parallel and on either side of the canal.

Current and Deposits. — The canal is always filling up and a constant expenditure of money is required for dredging. The importance of this factor is shown by the following figures on the cost of dredging taken from various reports:

1875	550 feet west and 500 feet east of Bond Street	$2,500.00
	At Third Street bridge	250.00
1876	No dredging.	
1877	Gowanus Canal	325.00
1878	Gowanus Canal at various bridges	1,995.00
	Gowanus Canal at Sackett Street	130.00
1879	Gowanus Canal at various bridges	1,995.00
	Gowanus Canal at various localities	513.00
1880	Gowanus Canal	1,019.70
1881–1884	No records.	
1885	From Douglass Street (7 feet at low water) to Hamilton Avenue (12 feet at low water)	16,450.00
1886–1893	No records.	
1894	From Butler Street to Union Street	2,980.00
1895	Entire length and width	7,527.00
	Soundings	37.75
1896	Dredging Gowanus Canal	990.00

1897–1901	No reports available.	
1902	Dredging	$5,051.00
	Engineering expenses	106.25
	Inspection	222.50
	Total of all available records	$42,092.20

At present barges at the upper end of the canal are aground at low tide. The depth of the canal is now inadequate for the passage of fireboats.

The mere rise and fall of the tide have apparently no purifying effect whatever, and do not prevent the filling up of the canal with the heavier portions of the sewage. Only after heavy rainstorms, when a large amount of water is discharged from the storm sewers, is there any current noticeable.

Appearance and Odors. — The surface of the water in the canal is covered with a layer of oil, coal dust, and scum. Gases are constantly seen bubbling up through the water, especially at the upper end of the canal. In the summer time the stench at the canal is unbearable, and it is noticed at all times a block away. On certain days not only the immediate locality, but also large sections of the city on the north, west, and east, according to the direction of the wind, are seriously affected. The section on the west was formerly a handsome residence district, but in part owing to this annoyance property has steadily declined in value in the past twenty-five years.

Investigation of the Sanitary Conditions

This investigation was undertaken to learn as much as practicable within a limited time regarding the character of the water now filling the Gowanus Canal and the nature of the pollution now entering it.

In a general way all this work has been undertaken to answer as clearly as possible the following questions:

1. Are all the odors due to the canal or are they due to manufacturing plants along the sides?

2. What is the character of the water which now fills the canal? What is the amount of organic matter present and the amount of oxygen necessary to destroy it? Are there any chemical wastes which inhibit the reduction or oxidation of putrescible substances? What is the amount of those substances which appear to be indifferent to chem-

ical changes, but which silt up the canal? How does the canal water compare with unpolluted sea water? How does it compare with the water in that part of the harbor adjoining its outlet?

3. What is the character of the entering pollution from the factories? Which is the larger factor in bringing about pollution, industrial wastes or sewage?

4. Do the ebb and flow of the tide renew the water in the canal, or does much of this water flow back and forth?

5. Is the water continually active in digesting or oxidizing and capable of rendering innocuous the pollution that comes into it?

6. What is the proportion of sewage, fresh water, and salt water in the canal; that is, what is the sewage density or the quantity of sewage per cubic foot of water?

7. What quantity of East River water would be required to dilute sufficiently the daily discharge? What quantity will be required to flush out the present contents of the canal if dredging is first resorted to?

This report will be divided into five parts:

1. The sanitary inspection.
2. Chemical and bacteriological analyses, with their interpretation.
3. Summary of existing conditions.
4. Recommendations, with calculation of the water to be pumped.
5. Summary and conclusions.

The Sanitary Inspection

As careful an inspection as the time would permit was made, especial attention being paid to the incoming sewers and resulting conditions. The canal in its present state is exceedingly obnoxious, the stench even in the winter time being very disagreeable. The water is black, warm, and foul. No fish have been caught in the canal for many years. There is practically no current. The appearance of the surface and bulwarks is disgusting, especially near the sewer outlets.

The surface of the canal is covered with scum. In the upper portion (Fig. 9) this is characteristic of domestic sewage, such as grease and slime, partially disintegrated human fæces, and other organic matter. The lower portion of the canal from the Bond Street sewer outlet to Gowanus Bay is covered with unsightly patches of floating rubbish

which have been accumulated by the action of the tugboats, wind, and tide. These patches consist largely of brown and yellow oily substances, which spread out in thick layers on the water surface and seem to gather up all the other floating *débris*, such as waste paper, fecal matter, melon rinds, banana skins, kitchen refuse, tin cans, broken boxes, coal dust, and other matter.

The water throughout the canal is exceedingly turbid, especially at the upper end. The turbidity is so great that the water is of a light gray color. The color becomes darker, however, and the turbidity

FIG. 9.— VIEW LOOKING NORTH FROM UNION STREET BRIDGE SHOWING LAYER OF SCUM IN THE FOREGROUND

less as the outlet is neared. In no place in the canal is it possible to see the oar blades when in a rowboat.

Practically all the plants along the canal discharge directly into it, but the amount of sewage from these is small when compared with that contributed by the city sewers. Not only is the discharge of the sewers greater than that of the factories, but its amount and its offensive character are shown by the bad condition of that part of the canal into which it discharges. These sewers have all been named in the first part of this report. All the so-called "storm sewers" in dry weather discharge concentrated sewage, as the chemical analyses will show. The chief

offender, however, is the 15-foot relief sewer at the head of the canal. During the quieter hours of the day the depth of the dry weather flow in this sewer is about 6 inches. This is continually bringing down waste paper, hair, and other sewage stuff. White scum covers the water surface in front of its outlet. Slaughterhouses drain into this sewer, for at times large quantities of blood are discharged. On wash days suds are in abundance.

A large silt basin was provided at the head of the canal to settle out the solid matter and detritus carried down in the storm sewers during heavy rains. A photograph of the silt basin is shown in Figure 8. The settling basin, however, intercepts only the coarse, heavy material. The finer material passes through and silts up the canal. In October the canal was dredged from Union Street to the head end. By February the deposit in front of the outlets filled up this section of the canal to approximately 5 feet below mean low water. In April the top of this bank was only about 3 feet below. The conditions are such that at low tide all the canal boats are aground in this portion of the canal.

The continuous discharge of the Bond Street sewer was easily detected by means of the brown and yellow oily substance already referred to. This sewer has two 36-inch outlets.

Among the more conspicuous of the private sewers are those of the gas works, which continually discharge a yellow-brown liquor. There are several of these gas plants. Their discharge outlets are from 8 inches to 12 inches in diameter and discharge full. It is to this, doubtless, that the tarry incrustation of the posts and bulwarks of the canal is due.

Much hot water is discharged into the canal. In cold weather this causes a heavy fog to hang over it. The large amount of vapor given off and the constant bubbling up of gases make the canal look boiling hot. In February the temperature of the water was 65° F. at the head of the canal. This gradually became higher on going down the canal, until at Carroll Street, where a large power plant is located, it became 70°. From here to the First Street basin the temperature rapidly became higher until 90° F. was reached. On going down the canal this soon dropped again to 70° F. and then gradually diminished, until at the entrance to the bay it became 44° F. In April the temperatures were a little higher, but varied in the same way.

The semi-liquid layer of sludge at the bottom requires merely a

slight rise of temperature to cause the development of gases, which bubble up in practically the whole length of the canal. At the head end the bubbling is violent. Black solid matter arises to the surface, and discharging its burden of gas again disappears from view. The white scum at the head end is blackened and the smell is rank, becoming unbearable when the water is stirred up by the tugboats.

To sum up: The canal is an open sewer, or rather, in its present state, practically a septic tank. There is almost no current and the tide appears to exert no flushing effect whatever. Of the plants along the canal, the gas works are doubtless the chief offenders. The trouble, however, is due largely to the discharge from the city sewers, which discharging into a body of quiet water cause heavy deposits to be formed. The canal water being stagnant and devoid of oxygen, the deposits putrefy and are the seat of the nuisance. These conclusions are borne out by the chemical and bacteriological analyses.

Chemical and Bacteriological Analyses

Before taking up the regular analytical work, it was thought best to ascertain from a few preliminary samples from various portions of the canal the character of the water to be analyzed.

Two of these samples, one taken at the Union Street bridge near the head of the canal, and the other at the Ninth Street bridge near the lower end, gave interesting results. The first was strongly indicative of sewage, the other of industrial wastes. Tests were made for acidity. The first was found to be neutral to litmus, acid to phenolphthalein, and alkaline to methyl orange. The other, although neutral to litmus, was acid to both phenolphthalein and methyl orange. Both were decidedly turbid and had much matter in suspension. The behavior on evaporation on the steam bath and on ignition also deserves attention. The first blackened readily on ignition and gave off a strong sewage odor. The second on the bath gave off an acetic acid odor; on ignition the solid matter decrepitated, and the odor was at first leathery, then like fertilizer, and finally very offensive. The substance burned with great difficulty, indicating vegetable carbon. Both samples contained a large amount of chlorine and sulphates, the second, however, in much greater proportions than the first.

Pollution by the gas plants was particularly evident, both from the odor of the water and from the color and behavior of the precipitate formed on nesslerization. This, instead of being of the reddish color

characteristic of ammonia, was a heavy, curdy precipitate, canary yellow in color, the reaction indicating amines.

It was decided in the regular series of analyses to make the following six tests chemically: oxygen consumed, total organic nitrogen, free ammonia, dissolved oxygen, turbidity, and chlorine. From ratios of these six in sea water and sewage an attempt has been made to determine the degree of pollution of the canal.

Method of Taking Samples. — In obtaining samples care was taken to choose representative points along the canal and to guard against accidental or abnormal conditions. The samples were taken from a rowboat at different depths and at different points in a cross-section of the canal. This was done by letting up and down a large bottle with a double perforated stopper while rowing across the canal. The contents of the bottle were then emptied into a pail and a liter bottle was filled from the mixture. This method gave a sample which was fairly representative of the cross-section of the canal from which it was taken.

As soon as the samples for the entire canal were obtained they were immediately taken to the Mount Prospect Laboratory, which was within twenty minutes' ride from the canal.

Methods of Chemical and Physical Analysis. — With the exception of the test for turbidity, the methods of chemical and physical analysis were those recommended by the Committee on Standard Methods of Water Analysis. The oxygen consumed was determined by the five-minute-boil method, the nitrogen content by the Kjeldahl Process, and the free ammonia by direct nesslerization. The turbidity was determined by means of the Jackson turbidimeter. The observation was made by pouring the sample of water into the tube until the image of the candle disappeared. The turbidity was then read from a graduation on the side of the tube. This graduation corresponded to the turbidity produced in distilled water by a certain number of parts per million of silica standard.

Methods of Bacteriological Analysis. — The media used for this work were standard media, made according to the procedure established by the Committee on Standard Methods of the American Public Health Association. The determinations were made for total count per cubic centimeter by plating on gelatin at 20° C., body temperature count on litmus lactose agar at 37° C., and tests on gas production, the latter being the only tests for *B. coli* considered necessary. In plating, two dilutions, one to 1,000 and one to 10,000, respectively, were made.

In the first series of analyses, use was made of the method of direct

inoculation of 1 c.c. of the canal water into the Smith fermentation tube, but in a second series this method was abandoned in favor of Dr. Jackson's new bile media.[1]

Tests for Bacillus coli. — In the fermentation tubes 25 per cent. to 70 per cent. gas was considered indicative of the colon bacillus, and a positive record was made if the other tests were favorable, *i. e.*, if the proportion of CO_2 fell within the right limit. This limit was from 25 per cent. to 40 per cent. absorption by caustic.

First Series of Analyses

Dissolved Oxygen. — Examinations of the water for dissolved oxygen were carried on simultaneously with the sanitary inspection. About thirty samples were taken at intervals along the canal from the head end to Hamilton Avenue, and, with the few following exceptions, negative results were obtained. Four surface samples also were taken from the East River, and the results of analysis are given in the second table below.

Gowanus Canal

No.	Place of collection.	Temperature.	c.c. oxygen per liter.	Per cent. saturation.
1	Entrance to power house basin, 4 P.M.	80° F.	1.14	20.2
2	East pier, Third Street bridge, 4 P.M.	70° F.	0.58	9.3
3	Entrance power house basin 9 A.M. next day	90° F.	1.54	30.4
4	Just below basin	90° F.	1.05	20.7
5	Above Third Street bridge	70° F.	1.03	16.5
6	Below Third Street bridge	70° F.	1.01	16.2
7	20 feet below Third Street bridge	70° F.	0.73	11.7
8	75 feet below Third Street bridge	70° F.	0.30	4.8
9	100 feet below Third Street bridge	70° F.	0.00	0.0

East River

No.	Place of collection.	Temperature.	c.c. oxygen per liter.	Per cent. saturation.
1	Buttermilk Channel, 200 feet from Brooklyn side	35° F.	7.50	77.4
2	Mid-stream opposite Governor's Island	30° F.	7.58	74.5
3	Return trip, same as 2	30° F.	7.95	78.0
4	Buttermilk Channel, 75 feet from Brooklyn side	34° F.	7.90	80.5

[1] For description, see Biological Studies by the Pupils of William Thompson Sedgwick, Boston, 1906, pp. 292–299.

The other results of the first series are shown in tabulated form in Table I.

Analysis of the Sludge. — Samples of the sludge which appeared to form a semi-liquid layer on the bottom were analyzed for total solids, oxygen consumed, and total organic nitrogen Inasmuch as the method of taking samples was crude and allowed some water to mix with the sludge, the density was changed. The results are therefore expressed in ratios for comparison.

Location of sample.	Oxygen consumed : total nitrogen.	C + N : total solids.
Head of canal	16.2	1 : 1.9
150 feet below head	13.0	1 : 2.0
300 feet below head	9.8	1 : 2.2
Opposite Degraw Street	11.0	1 : 2.1
Entrance First Street basin	10.3	1 : 3.3
Entrance Fifth Street basin	7.0	1 : 3.1
Opposite Bond Street	13.0	1 : 3.5

Experiments were made on the temperature necessary to develop gases from the sludge. Ten c.c. of the various samples were diluted to about 60 c.c. and placed on ice. After standing on the ice for several hours, all the foul air possible was exhausted and replaced by fresh air. The bottles were then set back into the ice chest and allowed to remain there over night. The temperature of the ice chamber was 2° C. At this temperature no sewage odor was noticeable. The samples were then allowed to stand in the room, and their condition was noted from time to time. No. 1 became offensive at 12° C.; Nos. 2, 3, and 4 at 12.5° to 13° C. Sample No. 5 contained a quantity of tarry matter and required a temperature of 14° C. to become offensive. The samples were then slowly warmed. At 20° C. the odor was very strong. At 23° C. the stench became vile and unbearable, especially in the first three samples.

A sample of the incrusting substance on the bulwarks was also taken. On analysis this was found to be a tarry waste product of the gas works.

Second Series of Analyses

The first series of analyses was made in February, 1906. The second was carried out in April. This series included a sample of

TABLE I. — SHOWING ANALYSIS OF SAMPLES TAKEN FROM THE GOWANUS CANAL, FEBRUARY 3, 1906

CHEMICAL ANALYSIS (Parts per Million)

No.	Place of collection.	Temperature.	Turbidity. (Parts per million of silica.)	Nitrogen as		Chlorine.	Oxygen consumed.	Number of bacteria per c.c., 48 hours at 20° C.	B. Coli In 1 c.c.
				Total organic nitrogen.	Free ammonia.				
1	Head of canal	. .	420	50.4	17.0	300	95.3	3,220,000	-
2	Just below Degraw Street	. .	265	44.0	17.0	1,400	64.0	1,440,000	+
3	Just below Carroll Street	. .	100	12.2	7.0	4,000	46.4	252,000	+
4	Entrance First Street basin	90° F.	105	10.4	4.4	5,700	36.8	99,000	+
5	Entrance Fifth Street basin	.	125	8.2	6.6	5,900	43.2	171,000	+
6	Opposite Bond Street	. .	95	10.4	4.4	6,400	28.8	168,000	+
7	In Sixth Street basin	. .	160	14.7	6.1	6,200	45.6	217,000	+
8	Entrance Eighth Street basin above tartar factory	. .	100	15.9	3.3	6,700	42.4	217,000	+
9	Below Ninth Street	65° F.	90	13.9	5.3	7,000	35.2	254,000	+
10	Below Hamilton Avenue	55° F.	110	4.8	4.8	7,450	56.8	90,000	+
11	Entrance to bay	44° F.	120	13.5	5.7	7,500	102.4	69,000	+

NOTE. — Samples were taken at time of flood tide.

sewage taken from a manhole at the corner of Nevins and Butler Streets, and fifteen samples taken from different portions of the canal. The sample from the manhole was taken on Saturday morning, April 14. The depth of flow in the sewer was 6 inches. The samples from the canal were not taken until Monday morning, April 16. A heavy rain fell on Saturday night and Sunday morning, and the canal water was well stirred up.

In this series samples were analyzed both filtered and unfiltered, and the test for total solids was added. In the latter the sodium chloride present rapidly took on moisture from the air, and for that reason the tests for total and dissolved solids are rough and therefore of not much importance. The results of the second series are given in tabulated form in Table II.

Tests for putrescibility of the sewage and the degree of dilution necessary were made by the methylene blue test. This was done by adding 1 c.c. of a 0.1 per cent. solution of methylene blue to a half pint of the different dilutions of the sewage with tap water. These tests showed a dilution of one part sewage to fifteen parts water to be necessary for a stable mixture.

Interpretation of the Results

Interpretation of Figures Obtained. — The tabulated results give evidence of the amount and nature of the pollution. Tables, however, show more when they are represented graphically. Therefore to aid in the interpretation the results obtained have been plotted. The construction of the diagrams needs no explanation. The curves are striking and interesting. With the exception of those for chlorine and total and dissolved solids, they all have a general downward tendency, which shows the effect of dilution with sea water. The curves for the first series are much smoother than those for the second, because the second series of samples was taken after the canal had been stirred up by a heavy rainfall. It will be interesting to examine the curves and to account for the variations which occur.

Total Organic Nitrogen. — In the first series (Fig. 10) this curve falls rapidly until Bond Street is reached. Here it again rises, reaching a maximum opposite the Tartar Chemical Company.

In the second series (Fig. 12) there is a general decrease. The curve drops rapidly at the entrance to the First Street basin. This is

TABLE II. — SHOWING ANALYSIS OF SAMPLES TAKEN FROM THE GOWANUS CANAL, APRIL 16, 1906

CHEMICAL ANALYSIS (Parts per Million)

No.	Place of collection.	Temperature.	Turbidity (parts per million of silica).	Nitrogen as: Organic nitrogen: In solution.	Nitrogen as: Organic nitrogen: In suspension.	Nitrogen as: Organic nitrogen: Total.	Nitrogen as: Free ammonia.	Total solids.	Suspended solids.	In solution.	Chlorine.	Oxygen Consumed: In solution.	Oxygen Consumed: In suspension.	Oxygen Consumed: Total.	Number of bacteria per c.c., 48 hours at 20° C.	B. Coli: In 0.1 c.c.	B. Coli: In 1 c.c.	B. Coli: In 10 c.c.
	Sewage taken from manhole, corner Nevins and Butler Streets, April 14, 1906, 9 A.M.	. .	475	51.8	19.5	71.3	36.0	1,860	1,220	640	230	116.4	48.6	165.0	3,120,000	+	+	+
1	Head of canal	77°.0 F.	380	30.5	19.3	49.8	24.0	1,160	260	900	350	42.3	33.2	75.5	—	+	+	+
2	Opposite Sackett Street	77°.0 F.	320	17.8	25.7	43.5	11.0	3,580	320	3,260	1,010	48.6	37.4	86.0	1,680,000	+	+	+
3	Below Carroll Street	99°.5 F.	1,000	8.8	22.5	31.3	4.0	11,980	480	11,500	4,600	17.6	91.7	109.3	1,280,000	+	+	+
4	Entrance First Street basin	101°.3 F.	150	9.8	1.6	11.4	3.0	10,720	1,260	9,460	4,700	16.2	9.2	25.4	1,030,000	+	+	+
5	Above Third Street	91°.4 F.	400	5.3	12.8	18.1	4.3	12,380	620	11,760	4,600	17.6	67.8	85.4	685,000	+	+	+
6	Opposite Fifth Street basin	73°.4 F.	265	24.8	12.8	37.6	4.0	10,540	2,440	8,140	4,850	14.1	32.4	46.5	670,000	+	+	
7	Below Bond Street	. .	385	8.8	4.8	13.6	4.0	15,540	6,600	8,940	3,890	20.4	57.1	77.5	643,000	—	—	
8	Opposite Sixth Street basin	. .	155	7.8	1.0	8.8	4.0	7,100	380	6,720	3,100	16.9	7.1	24.0	360,000	+	—	
9	Above Seventh Street basin	55°.4 F.	160	8.3	2.6	10.9	3.5	11,300	1,820	9,480	4,100	12.7	8.5	21.2	228,000	+	+	+
10	Below Seventh Street basin	. .	175	19.9	6.4	26.3	2.5	9,500	180	9,320	4,200	12.7	7.0	19.7	223,000	+	+	+
11	Below Ninth Street	. .	290[1]	6.8	3.2	10.0	6.0	9,480	780	8,700	4,480	14.8	4.9	19.7	219,000	+	+	+
12	Above Eleventh Street basin	. .	90	7.1	3.2	10.3	2.5	21,040	1,660	19,380	4,050	16.2	9.2	25.4	—	+	+	+
13	Above Hamilton Avenue (near sewer outlet)	. .	85	0.7	0.4	1.1	8.5	17,720	540	17,180	5,100	6.9	3.0	9.9	—	+	+	+
14	Below Hamilton Avenue (opposite sewer outlet)	51°.8 F.	80	6.0	4.8	10.8	2.0	24,320	12,360	11,960	5,200	13.3	5.0	18.3	296,000	+	+	+
15	Entrance to bay	50°.0 F.	70	. .	. .	9.3	3.5	19,900	6,360	13,540	6,950	7.1	7.7	14.8	335,000	+	+	+

NOTE. — Samples taken on a rising tide.

[1] Milky.

due to the large amount of clean water discharged from the power house. At Third Street the curve rises to what would be a point on the normal dilution curve. Opposite the Fifth Street basin there is a rapid rise, which is due to a stirring up of the water at that point by tugs at the time that the sample was taken. The curve then again drops rapidly,

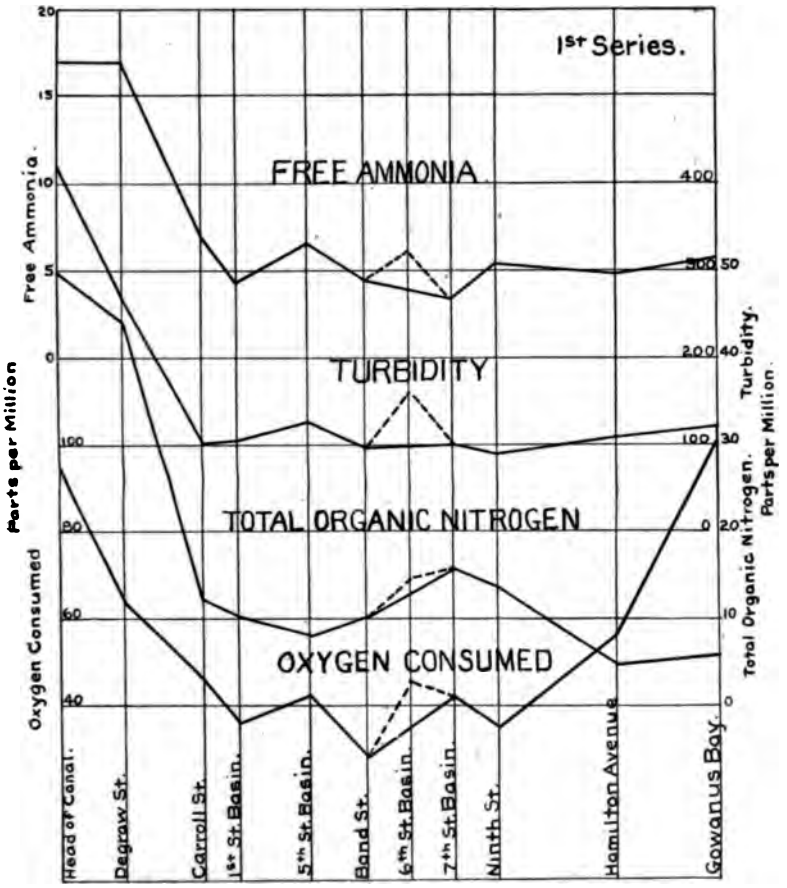


FIG. 10

but not to what would be a point on the normal dilution curve. The Bond Street sewer enters here. There is then a gradual drop until we arrive at the Tartar Chemical Company, where there is a sudden increase. Above Hamilton Avenue bridge there is another quick drop. A glance at some of the other curves shows that this drop is general. On the other side of the bridge, however, the curve rises again.

A sewer enters here. There is then a slow, gradual decrease, indicating dilution with sea water.

The curves for suspended and dissolved organic nitrogen are similar to that for the total organic nitrogen, and no special comment on them is necessary.

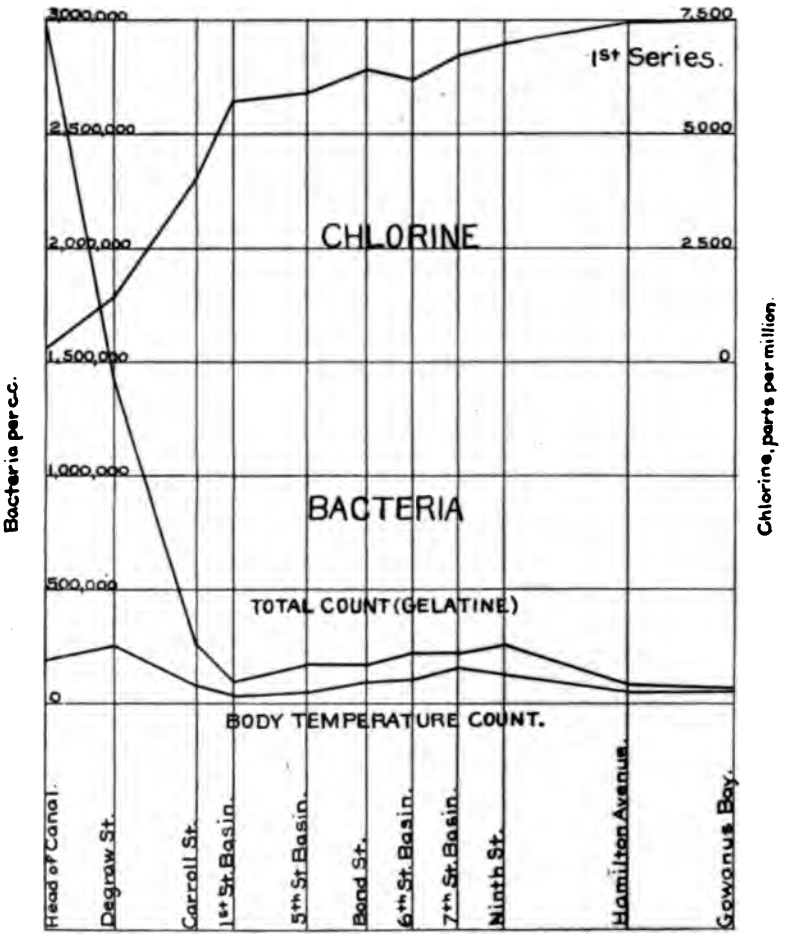


FIG. 11

Oxygen Consumed. — In the first series (Fig. 10) this curve falls off rapidly until after Bond Street is passed. Opposite the Fifth Street basin there is an increase, probably due to coal dust. The most conspicuous part of the curve, however, is the steady and rapid increase after the starch factory at Ninth Street is passed.

In the second series (Fig. 13) there is an increase at the start, with a quick rise at Carroll Street. A glance at the turbidity curve will show that this rise is due to the water having been stirred up. There is a quick drop at the First Street basin and a quick rise again at Third Street. The turbidity also is high at this point. The appar-

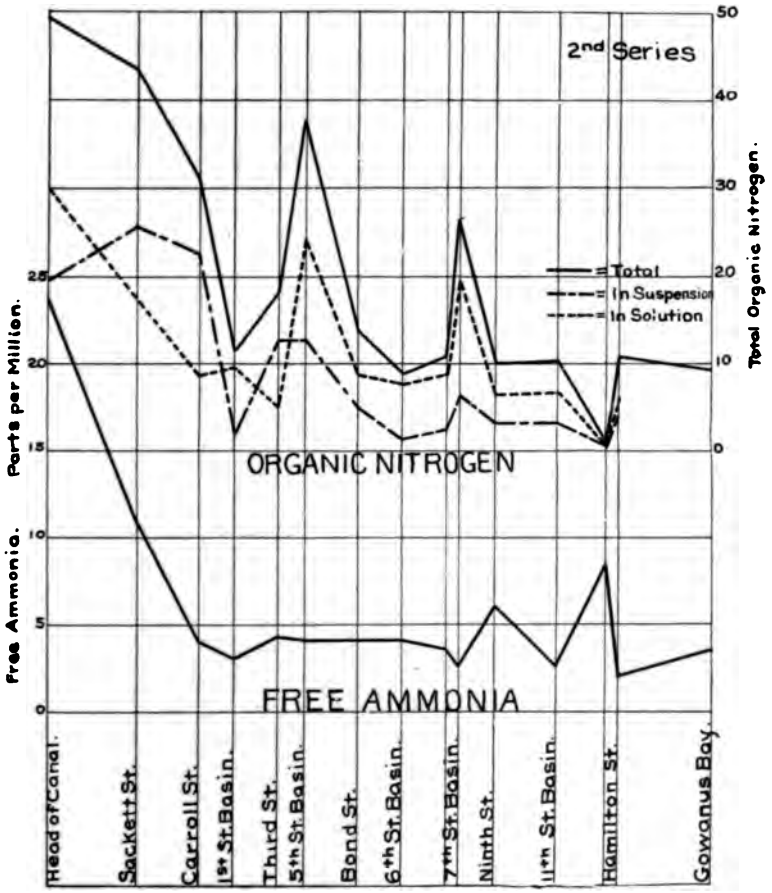


FIG. 12

ent drop at the Fifth Street basin was unexpected, since the nitrogen is high at that point. A further study of the diagrams, however, will show that the oxygen consumed is also absolutely very high.

After passing Bond Street the curve has a downward tendency, with only a slight rise beyond Ninth Street. This is significant. The samples were taken on a Monday morning, and there was no pollution

then by the starch factory. Most of the material which had been discharged on Saturday night was flushed out by the heavy flow of storm water on Saturday night and Sunday.

The same drop just above the Hamilton Avenue bridge already

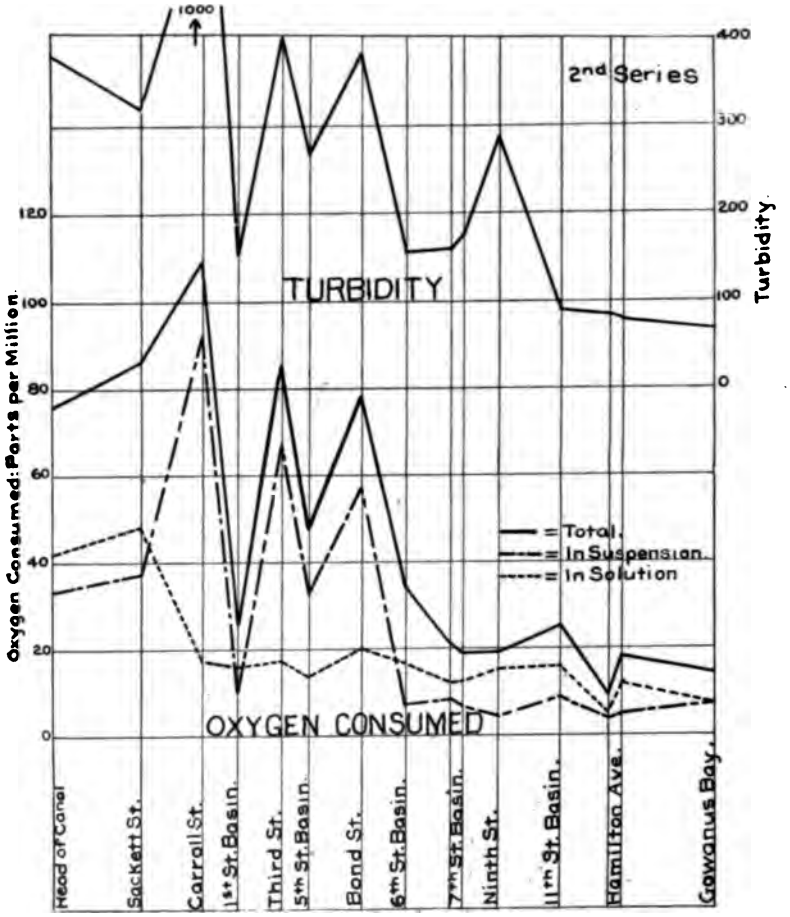


FIG. 13

mentioned in the discussion of the organic nitrogen curve is conspicuous here. Below Hamilton Avenue the curve rises again and then decreases gradually.

Turbidity. — In both series of analyses (Figs. 10 and 13) this curve seems to vary with the dilution and shows that sedimentation has taken

place all the way down, being interrupted occasionally by the stirring up of the water. The curves for turbidity are strikingly similar to those for organic nitrogen and for oxygen consumed.

The remaining curves simply reënforce points brought out in the

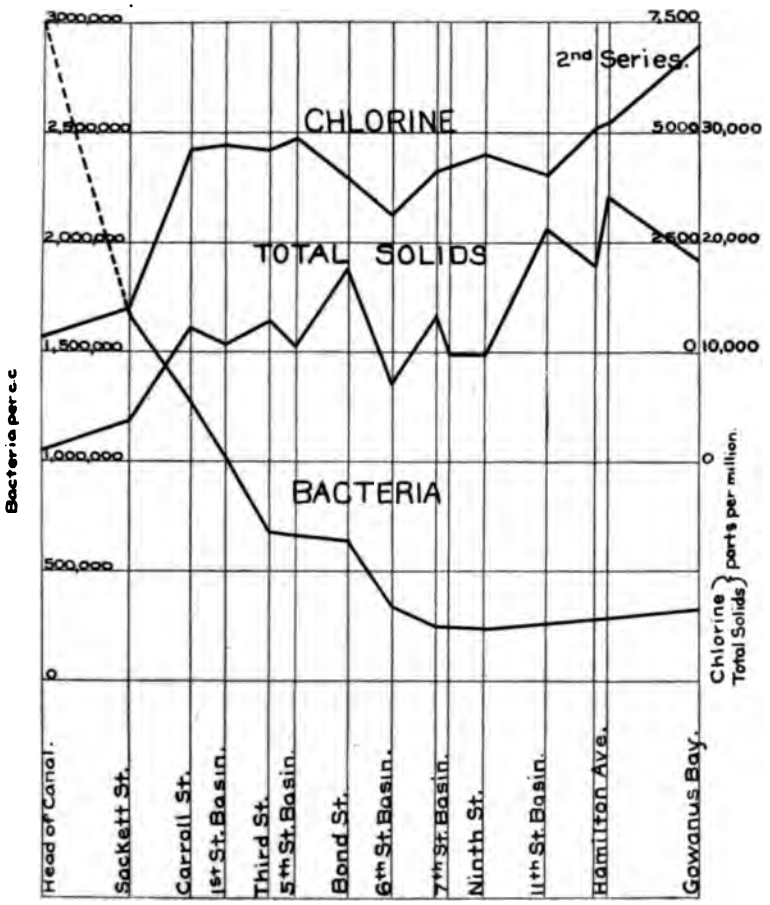


FIG. 14

curves already discussed and require no especial explanation. We are, therefore, ready to consider the various curves simultaneously. Sample No. 1 shows at once that we have much accumulated solid matter which is constantly stirred up. The nitrogen is very high. This means that there is an additional supply of organic matter there, which, being constantly stirred up, keeps in circulation, but is never carried out. This

effect is not lost all the way down the canal. The fact that the chlorine is above the normal — twice what it ought to be — shows a mixture of sea water with the sewage. In the first five samples the ratio of dissolved nitrogen to total nitrogen gives good evidence of septic action. Since organic nitrogen is converted into free ammonia, there are two changes noticeable: the ratio of free ammonia to total organic nitrogen and the ratio of oxygen consumed to total organic nitrogen becomes greater. Both carbon and nitrogen are going down, but the nitrogen goes down much faster.

From a bacteriological standpoint, the low count at body temperature as compared with the high total count in water from the head of the canal is interesting. It indicates that septic action is taking place and corroborates the evidence mentioned in the last paragraph.

The total number of bacteria falls off very rapidly on going down the canal, reaching in the first series of analyses (Fig. 11) a minimum opposite the First Street basin. In the second series (Fig. 14) this minimum is not reached until the Seventh Street basin is reached, showing the flushing effect of the storm water. A glance at the curves for chlorine shows that this rapid decrease in the total bacteria count is due to dilution.

Below the First Street basin the number of bacteria does not increase materially, thus substantiating the evidence that most of the pollution below this point is due to industrial wastes.

The discharge of the Bond Street sewer seems to increase the oxygen consumed, but not the nitrogen. The bacteria go down, and this sewage seems to be an antiseptic, non-nitrogenous substance, in appearance quite similar to gas plant wastes.

Lateral Basins. — In the first series, to ascertain how the water in the basins compared with that in the main part of the canal, a sample was taken from one of these. This is represented in the curve (Fig. 10) by dotted lines. The result is significant. A glance at the curves shows that free ammonia, oxygen consumed, total organic nitrogen, turbidity, and the total bacteria count are higher than in the adjacent portion of the main canal, while the chlorine and the body temperature count are lower. This is characteristic of a dead end. The depression in the chlorine curve shows that the tide exerts no flushing effect, and the low body temperature count shows that the water in the basin is stagnant.

Variations between the Two Series. — The first series of analyses was carried on at a time when there was no rain. The second series

of samples was taken after the run off from a heavy rainfall had stirred up the contents of the canal. On comparing the two sets of curves, the reader will see that in general they cross one another several times, that the curves of the second series are very ragged, plainly giving evidence of a general stirring up. At the uppermost point of the canal, however, the second series shows less pollution than the first. The curves soon cross, however, and in general the first series of curves is lower than the second. This is due to the large volume of storm water which had pushed the sewage at the head end farther down. The turbidity curve for the second series is entirely above that for the first series.

Difference in Character of Pollution in Various Parts of the Canal.— The upper part of the canal is badly polluted by sewage. At the lower end the pollution is largely industrial wastes mixed with more or less sewage.

As a rule, the amount of nitrogen present varies directly with the amount of sewage. The other constituents of sewage vary with the nitrogen. Therefore when the nitrogen is greatly increased without a corresponding increase in the other sewage substances it is an indication of industrial wastes. This is exactly what happens in that portion of the canal opposite the Tartar Chemical Company. On talking with one of their employees, we learned that crude argol is digested with sulphuric acid, and that the waste product is an acid sludge running high in sulphates and nitrogen.

In the first series, below Ninth Street the oxygen consumed curve went up rapidly. In the second series the curve had a downward tendency. The starch factory, not running on Sunday, had no waste to discharge at that time. The abnormal values for the oxygen consumed are probably due to gluten in the wastes discharged by the starch factory.

Another interesting point, characteristic of both series of curves, is the sudden drop in most of the curves just above Hamilton Avenue. It is significant that not only the organic nitrogen, oxygen consumed, turbidity, and total solids, but the bacteria also go down. This looks like precipitation. The curves for ammonia and chlorine, on the other hand, show a slight increase. Immediately above this point is a coal gas plant, which evidently uses lime to recover its ammonia. The waste from the Tartar Chemical Company, which is carried along by the tide, comes into contact with the gas plant waste, and calcium sulphate is

probably precipitated, carrying down with it nearly all the other suspended matter.

The rapid decrease in bacteria below Bond Street gives evidence of antiseptic action. A glance at the diagrams will show that, although the nitrogen and carbon go up at that point, the ammonia remains the same, and the bacteria count goes down and stays down. The fact that the ratio of carbon to nitrogen is greatly increased shows that the pollution from the Bond Street sewer is largely of a carbonaceous nature.

Although taken at different times, and thus representing different conditions, there is no essential difference in the results obtained from the two series. The second series simply reënforces the first and justifies drawing the following conclusions:

The canal is highly polluted with house drainage and industrial wastes. The city sewers are the chief source of the trouble. The organic animal matters contained in the sewage are more easily susceptible to putrefactive influences than is the vegetable matter in the industrial wastes. The tide exerts very little flushing effect in the main body of the canal, and practically none whatever in the dead ends or basins.

Summary of Existing Conditions

The table below will show the immense pollution of the canal. The figures for sea water were taken from the Report of the Committee on the Charles River Dam. The figures for Boston tap were taken from the Massachusetts Board of Health Report for 1904. Those for harbor water are the average of the accompanying table, compiled from analyses made by Dr. Jackson for the New York Bay Pollution Commission.

Sample.	Free NH_3.	Organic nitrogen.	Oxygen consumed.
From head of canal	24.0	50.1	85.4
Sea water	0.012	0.16	. .
Boston tap	0.015	0.29	3.9
Harbor water	0.534	1.28	. .

The figures speak for themselves. The pollution of the canal is almost fifty times that of the harbor.

TABLE III.— SHOWING ANALYSIS OF SAMPLES FROM THE EAST RIVER, MADE BY DR. DANIEL D. JACKSON FOR THE NEW YORK BAY POLLUTION COMMISSION

CHEMICAL ANALYSIS (Parts per Million)

No.	Date of collection.	Place of collection.	Temperature.	Turbidity (parts per million of silica).	Tide.	Nitrogen as			Chlorine.	Dissolved oxygen; c.c. per liter.	Number of bacteria per c.c., 48 hours at 20° C.	B. Coli		
						Albuminoid ammonia.	Free ammonia.	Nitrites.				In 0.1 c.c.	In 1 c.c.	In 10 c.c.
	April 1, 1905, A.M.													
1	9.55	Off Battery (bottom)	—	7	Flood	0.27	0.31	. .	11,800	8.02	4,280	+	+	+
2	10.00	Off Battery (surface)	—	10	Flood	0.27	0.32	. .	6,100	8.84	6,250	+	+	+
3	10.05	East River off Pier No. 15	. .	10	Flood	—	—	. .	4,800	. .	4,410	+	+	+
4	10.10	Under Manhattan Bridge	—	8	Flood	0.32	0.49	. .	9,600	. .	8,460	+	+	+
	Jan. 30, P.M.													
9	12.35	Off Battery and Governor's Island (midstream, 5 feet from surface)	37°.0 F.	45	Flood	0.78	0.97	0.012	7,600	8.50	1,510	+	+	+
8	12.30	Off Battery and Governor's Island (midstream, 40 feet from surface)	37°.0 F.	30	Flood	0.73	0.84	0.015	11,600	—	920	+	+	+
7	12.20	Off Battery and Governor's Island (midstream, 80 feet from surface)	37°.0 F.	35	Flood	0.73	0.75	0.012	12,700	—	760	+	+	+
12	3.15	Off Battery and Governor's Island (midstream, 5 feet from surface)	. .	18	Ebb	0.73	1.11	0.013	9,100	8.60	1,200	+	+	+
11	3.10	Off Battery and Governor's Island (midstream, 40 feet from surface)	. .	20	Ebb	0.67	0.70	0.012	13,100	—	740	+	+	+
10	3.00	Off Battery and Governor's Island (midstream, 80 feet from surface)	. .	25	Ebb	0.71	0.72	0.011	13,200	—	540	+	+	+
		Series No. 6												
27	3.38	Off Battery	33°.0 F.	6	. .	0.28	0.36	. .	8,300	. .	7,280	+	+	+
28	3.45	Off Pier No. 6, East River	33°.5 F.	—	. .	—	—	. .	8,400	. .	14,100	+	+	+
29	3.55	Off Pier No. 13, East River	33°.5 F.	10	. .	0.24	0.41	. .	8,600	. .	18,400	+	+	+
30	3.58	Off Pier No. 20, East River	33°.5 F.	5	. .	0.21	0.37	. .	8,900	. .	12,600	+	+	+
31	4.00	Off Pier No. 28, East River	33°.5 F.	7	. .	0.40	0.52	. .	8,400	6.98	15,300	+	+	+
32	4.05	Off Pier No. 23, East River (Brooklyn)	33°.5 F.	—	. .	—	—	. .	8,600	. .	4,300	0	0	+
33	4.15	Off Atlantic Docks, Buttermilk Channel	33°.5 F.	8	. .	0.25	0.40	. .	8,600	6.54	10,400	+	+	+
35	4.25	Gowanus Bay	. .	7	. .	0.35	0.74	. .	8,600	5.63	8,500	+	+	+
36	4.35	Gowanus Canal, Hamilton Avenue Bridge	. .	10	. .	1.11	7.00	. .	6,800	. .	270,000	+	+	+

Absolute Values Compared with Sewage. — Below is given a table comparing the canal water with several well-known sewages.

Place.	Date.	Free NH_3.	Organic Nitrogen.		Chlorine.	Oxygen consumed.	Bacteria per c.c.
			Total.	Solution.			
Brooklyn	April 14, 1906	36.0	71.3	51.8	230.0	165.0	3,120,000
Boston	Average	19.9	23.0	10.5	1,300.0	45.0	3,000,000
Lawrence	Maximum, 1904	71.8	39.2	20.6	163.9	65.4	3,020,000
Lawrence	Minimum, 1904	41.6	12.1	5.4	82.7	38.4	1,440,000
Lawrence	Average, 1904	51.5	18.3	8.7	123.1	48.6	1,930,000
Andover	June, 1902	103.0	51.4	20.0	678.0	107.7	3,680,000
Andover	Average, 1902	74.6	35.8	17.0	164.7	76.7	3,750,000
Head of canal	Mean	24.0	50.1	30.5	325.0	85.4	3,100,000
Opposite Fifth Street basin	Mean	7.5	37.6	24.8	4,850.0	46.5	670,000
Below Hamilton Avenue	Mean	3.5	7.8	4.5	6,325.0	18.3	200,000

From the above table it is evident that the water at the head of the canal is about two-thirds as strong as Brooklyn sewage. It is more than twice as strong as Boston sewage; its strength is three times that of Lawrence sewage and about equal to that of Andover, which is one of the strongest in Massachusetts.

The sample taken opposite the Fifth Street basin corresponds to the strongest Lawrence sewage in 1904, and to the average Andover sewage for 1902.

At Hamilton Avenue the water contains about one-tenth of Brooklyn sewage, and is about one-half the strength of the minimum Lawrence sewage in 1904.

Recommendations, with Calculation of the Amount of Water to be Pumped

Recommendations. — The Gowanus Canal is in a very poor sanitary condition, and measures should be taken to abate this nuisance as soon as possible. In the study from which this abstract is taken, the methods of dealing with this problem came under two heads, those which involve some method of flushing the canal and those involving a sewerage system for the locality. These were taken up and considered in detail by

the writer's colleague in the investigation — Mr. Norman P. Gerhard, now assistant engineer, Board of Water Supply, City of New York.

It is not the purpose of this abstract to suggest a remedy, since the problem has already received the attention of the engineers of the Borough of Brooklyn and a flushing tunnel from the East River to the head of the Gowanus Canal is now under construction. The writer will therefore confine himself, as he did in the original thesis, to a calculation of the amount of water to be pumped under various methods of flushing the canal.

Calculations were made in two cases. In the first it was assumed that flushing alone would be considered and enough water pumped in to render the sewage matter innocuous and to create a current strong enough to prevent it from settling out. In the second case it was assumed that intercepting sewers would be built and the district sewered, enough water being pumped to cleanse the canal in a reasonable length of time, and thereafter create a small current sufficient to prevent it from becoming stagnant.

Both methods require that the present sludge deposits should be removed by dredging. A tremendous quantity of water would be required to give sufficient scouring velocity to remove the sludge. Even so, the present nuisance at the head of the Gowanus Canal would only be transferred to its branch dead ends and into Gowanus Bay. The power of New York Harbor to dispose of the sewage that comes into it is already being questioned. The Harbor Pollution Commission found that the tide has little effect in eliminating the pollution of the bay, and that the water seems incapable of renewing its supply of oxygen. It is evident then that it would be unwise to pollute the harbor still more by flushing into it the sludge which has accumulated in the Gowanus Canal.

Calculation of the Amount of Water to be Pumped. — We have, therefore, to consider for calculation two possibilities, the daily dilution of the total amount of sewage discharged into the Gowanus Canal, and the remedying of its present unsanitary condition in case an intercepting sewer should be built. The object of these calculations is to compute the required dilution from figures obtained by chemical analyses. Before proceeding with these calculations it is necessary, however, to determine first the proportion of sewage at present in the canal.

Sewage Density. — This may be defined as the proportion of sewage per unit volume. The canal water can be considered as a mixture of

three separate liquids: sewage, terrestrial (*i.e.*, surface + ground) water, and harbor water. The object of these calculations is to obtain absolute values for each of these three. In making these calculations, use has been made of the usual method of determining by the chlorine content in a mixture of two such liquids the proportion of each. This gave two independent equations. A third equation was obtained by means of the nitrogen values. The method of attack was as follows:

Consider a section in the canal of unit dimensions. Let

x = portion of sewage;
y = portion of terrestrial water;
z = portion of harbor water;
C = total chlorine;
N = total nitrogen;
c_1 = chlorine in sewage;
c_2 = chlorine in terrestrial water;
c_3 = chlorine in harbor water;
n_1 = nitrogen in sewage;
n_2 = nitrogen in terrestrial water;
n_3 = nitrogen in harbor water.

We then have the equations:

$$x + y + z = 1. \tag{1}$$

$$xc_1 + yc_2 + zc_3 = C. \tag{2}$$

$$xn_1 + yn_2 + zn_3 = N. \tag{3}$$

To solve we must find or assume values for the constants. The pollution of the canal is so great that the amount of nitrogen in terrestrial water when compared with it is practically zero. Considering the proximity to the sea, we may assume 10 as an average value of the chlorine content of this water.

From the table given above, showing the analyses made by Dr. Jackson for the New York Bay Pollution Commission, it appears that average figures for the nitrogen and chlorine content of harbor water may be assumed at 1 and 8,600, respectively.

Considering the particular problem on hand, we therefore have the following constants:

$$c_1 = 230;\ c_2 = 10;\ c_3 = 8{,}600;$$

$$n_1 = 107;\ n_2 = 0;\ n_3 = 1.$$

Substituting these values in the above equations, the two following tables, showing the proportion of sewage, terrestrial water, and harbor water at different sections in the canal, have been computed:

FIRST SERIES

No. of sample.	C.	N.	Proportion of		
			Sewage.	Terrestrial water.	Harbor water.
1	300	67.4	.63	.36	.01
2	1,400	61.0	.57	.42	.01
3	4,000	19.2	.18	.35	.47
4	5,700	14.8	.13	.19	.68
5	5,900	14.8	.13	.14	.73
6	6,400	14.8	.13	.08	.79
7	6,200	20.9	.19	.03	.78
8	6,700	19.2	.17	.03	.80
9	7,000	19.2	.17	.03	.80
10	7,450	9.6	.08	.09	.83
11	7,500	19.2	.17	.03	.80

SECOND SERIES

No. of sample.	C.	N.	Proportion of		
			Sewage.	Terrestrial water.	Harbor water.
1	350	73.8	.69	.31	.01
2	1,010	54.5	.51	.35	.14
3	4,600	35.3	.32	.05	.63
4	4,700	14.4	.13	.33	.54
5	4,600	22.4	.13	.29	.58
6	4,850	41.6	.38	.05	.57
7	3,890	17.6	.16	.36	.48
8	3,100	12.8	.12	.51	.37
9	4,100	14.4	.13	.38	.49
10	4,200	28.8	.26	.24	.50
11	4,480	16.0	.15	.33	.52
12	4,050	12.8	.12	.42	.46
13	5,100	9.6	.08	.34	.58
14	5,200	12.8	.12	.28	.60
15	6,950	12.8	.11	.10	.79

Calculation of Quantity of Water to be Pumped. — One condition of the degree of dilution required to make sewage inoffensive is that the diluting water shall have a sufficient supply of free oxygen. The experiments made on Brooklyn sewage for putrescibility showed the dilution of 1 : 15 to be necessary.

The sewage discharged into the canal daily is estimated to be 793,000 cubic feet. The amount of water, therefore, to make this innocuous is 793,000 × 15 = 11,895,000 cubic feet per day. Allowing a factor of safety of 2, there would be required 23,800,000 cubic feet per day.

Supposing no sewage is allowed to enter the canal and its contents are to be flushed out in thirty days, we can calculate the necessary quantity of water as follows:

The average sewage density of the canal, as computed in the above tables, is 0.25. Therefore $x = \frac{10{,}000{,}000\ (0.25)\ (15)}{30} = 1{,}250{,}000$ cubic feet per day.

The amount of water to be pumped was also calculated by a method based on the amount of oxygen available from East River water and the average amount of oxygen consumed by water in the canal. Although there is no evidence that sewage requires oxygen equivalent to its oxygen consumed value to oxidize it under natural conditions, this calculation is interesting in that the two methods of calculation used gave practically the same result. For this reason the writer thought this calculation from chemical data might be of general interest, and has included it in this report.

This calculation was based on the assumption that the volume of the canal water and the amount of oxygen consumed by it bears some relation to the amount of water to be pumped and the free or dissolved oxygen in it. We can express this relation algebraically as

$$xO_d = KSO_c$$

where x = quantity of East River water to be pumped in cubic feet per day.

O_d = amount of dissolved oxygen in parts per million in the water to be pumped.

S = amount of sewage to be oxidized in cubic feet per day.

O_c = oxygen consumed by S in parts per million.

K = ratio of amount of dissolved oxygen in flushing water to amount required to oxidize the organic matter.

If O_d is all to be used up, K becomes unity, and the quantity to be pumped is $x = \frac{SO}{O_d}$.

It appears from analyses made of East River that 7.5 c.c. per liter is a fair average value for O_d.

Weight of liter O = 1.429 grams.
Weight of 1.0 c.c. O = 0.00143 gram.
Weight of 7.5 c.c. O = 0.0107 gram.

Therefore O_d = 10.7 parts per million and $x = \frac{SO}{10.7}$.

We will compute first the amount of water needed to render innocuous the sewage discharged into the canal. The total sewage discharged into the canal was estimated at 793,000 cubic feet per day. O_c = 165 parts per million. Therefore $x = \frac{793{,}000 \times 165}{10.7}$ = 12,200,000 cubic feet per day.

If we allow a factor of safety of 2 to cover future increase of sewage flow, x would equal 12,200,000 × 2 = 24,400,000 cubic feet per day.

The amount of water needed for flushing the canal, supposing no more sewage is allowed to enter and thirty days are allowed for flushing, was computed as follows. The volume of the canal water is 10,000,000 cubic feet. S in our formula would then be $\frac{10{,}000{,}000}{30}$ = 333,330 cubic feet per day. The average value for O_c is 46.1. Then

$$x = \frac{333{,}330 \times 46.1}{10.7} = 1{,}440{,}000 \text{ cubic feet per day.}$$

Summing up these calculations, it appears that if sewage is allowed to continue discharging into the canal perhaps 25,000,000 cubic feet of water will have to be pumped daily to dilute the canal water sufficiently to render it innocuous. If the district is to be sewered, 1,500,000 cubic feet per day will be necessary.

Summary and Conclusions

The Gowanus Canal in its present condition is unsanitary and a nuisance. Sewage enters the canal and stays there. The heavier particles settle out at once, forming banks in front of the outlets of the sewers. The light, flocculent matter moves up and down with the tide and is gradually deposited, silting up all portions of the canal.

The water being devoid of oxygen, this sludge then undergoes putrefaction. Inasmuch as the temperature of 65° to 70° F. is sufficient to cause the sludge to give off putrid gases and the average temperature of the canal even in the winter time is about 70° F., it is easily seen why the nuisance exists all the year round.

In proceeding to summarize the results from the special point of view of this investigation, an attempt will be made to answer the questions raised in the first portion of this part of this report.

The odors of the factories are distinct from those of the canal and are not offensive. The bad smells are due to the putrefaction of nitrogenous matter in the sewage and sludge.

The water which now fills the canal is a mixture of sewage, terrestrial, and harbor water. At the head of the canal the water is 0.65 sewage, 0.34 terrestrial water, and 0.01 harbor water. At Hamilton Avenue it is 0.10 sewage, 0.20 terrestrial water, and 0.70 harbor water. The average sewage density of the whole canal is 0.25. Brooklyn sewage is much stronger than Massachusetts sewages. The water at the head of the canal is slightly stronger than Andover sewage, and the average value of the whole canal corresponds very nicely to Lawrence sewage.

The amount of organic matter present is very large, and to destroy it would require an amount of oxygen equivalent to that contained in $\frac{10{,}000{,}000 \times 0.25 \times 165}{10}$ = say to 45,000,000 cubic feet of harbor water, which is about 75 per cent. saturated. The amount of putrescible substances present is large, and their oxidation is probably inhibited by antiseptic wastes contributed by the Bond Street sewer. The storm sewers bring down much matter which is indifferent to chemical change and which, silting up the canal, makes constant dredging necessary. The average of analyses on the sludge shows the amount of this to be about twice that of the organic matter present.

The pollution due to the factories is largely vegetable carbonaceous and nitrogenous organic matter. The Tartar Chemical Company and the starch factory contribute most of this. The amount of this waste, however, is small when compared to that contributed by the city sewers.

The canal water is about fifty times as much polluted as that in the part of the harbor adjoining its outlet; the ebb and flow of the tide do comparatively little toward renewing the water in the canal, the water in the latter practically simply surging back and forth.

The water required for pumping after dredging has taken place depends upon the method used. The amount required to render innocuous the sewage which is discharged into the canal and to provide for future increase is perhaps 25,000,000 cubic feet per day. To flush out the present contents in thirty days 1,500,000 cubic feet of East River water would be required daily. Therefore if flushing alone were resorted to 25,000,000 cubic feet per day are necessary. If the district is first sewered and the canal then flushed 1,500,000 cubic feet would be required daily.

THE DETECTION OF CARAMEL IN VANILLA EXTRACT

BY A. G. WOODMAN AND E. H. NEWHALL

THE detection of caramel when present in the small quantities used for coloring beverages, vinegar, or extracts is not a simple matter. Comparatively few methods have been proposed for this, and most of the tests are of a negative rather than positive character. Some of these negative methods have been shown to be of considerable value in such special cases as in distinguishing caramel from the natural color of whisky, but are not suited, necessarily, for such material as extract of vanilla. The only method given among the Official Methods of Analysis [1] is that depending on the color remaining after treatment with basic lead acetate, a method which, as will be shown later, is open to considerable objection. A thorough review of the literature indicated that the following methods were of value to study for use with extracts of vanilla: Of positive methods, precipitation with paraldehyde (the Amthor test) and precipitation with phenyl-hydrazine; of negative methods, depending in general upon the selective action of solvents or other reagents on the natural color, the fuller's earth test, and the test with basic lead acetate.

Preliminary Experiments.—Before studying the above mentioned methods in detail it was found advisable to review the action of the common organic solvents on caramel solutions, with the possibility of finding a solvent immiscible with water which would remove the caramel color directly from the extract. To this end, aqueous solutions of caramel were shaken in separate tests with ether, chloroform, petroleum ether, acetone, benzene, ethyl acetate, amyl acetate, ethyl benzoate, and carbon tetrachloride. In no case was any color found in the layer of added solvent. Of the solvents miscible with water only methyl alcohol and allyl alcohol had any appreciable solvent action. The use of methyl alcohol has already been proposed by Fradiss,[2] but it is necessary to

[1] U. S. Dept. Agr., Bur. of Chem., Bull. 107, p. 159.

[2] Ztschr. Zucker Ind., 28, 229.

employ it upon the dried residue. The solubility of caramel in methyl alcohol was found by experiment to be 8.232 grams per liter at 20°.

Paraldehyde Test.—This test, originally proposed by Amthor,[1] has found considerable application, especially in the examination of distilled liquors. In its original form it may be briefly summarized as follows: 10 c.c. of the liquid, contained in a tall, narrow glass, are mixed with 30–50 c.c. of paraldehyde, and absolute alcohol is added until the liquids are homogeneous. If caramel is present, at the end of twenty-four hours a brownish yellow or dark brown precipitate is formed.

A number of tests were made on solutions of caramel in studying the modifications of this procedure. It has been questioned whether the precipitate formed is caramel or a compound of caramel with paraldehyde. Experiment indicated, however, that the substance is in all probability caramel. It was brown and flocculent, resembling caramel in appearance. It was not sufficiently soluble to impart any color to warm methyl or ethyl alcohol when poured through the filter. In warm water, however, it was readily soluble, giving a dark brown solution. This solution had approximately the same reducing power on Fehling's solution as did a caramel solution of the same color. It is quite probable that the phenomenon observed in the paraldehyde test is only one of lessened solubility.

The relative volumes of paraldehyde and colored solution are matters in regard to which there appears to be considerable difference of opinion among those who have made use of the test. Experiments indicated that the paraldehyde should be largely in excess. For example, volumes of paraldehyde less than those of the caramel solution failed to give a precipitate within forty-eight hours. With equal volumes of paraldehyde and of caramel solution less than half the tests gave a precipitate within a day. The order in which the reagents were added had no effect on the results. In all of these experiments only sufficient alcohol to make the solutions homogeneous was added, as an excess of alcohol was found to be detrimental.

In regard to the effect of temperature on the precipitation it was found as a result of numerous trials that no advantage was gained by employing a temperature other than that of the laboratory.

The delicacy of the test is not very great. Tests made in triplicate showed that a precipitate can be obtained with a caramel solution of a

[1] Ztschr. anal. Chem., 24, 30.

concentration of 1 gram of caramel in 1,343 c.c. of water, whereas tests made with half that concentration failed. This would correspond to 0.00372 gram of caramel in the 5 c.c. used for the test.

To summarize, repeated trials showed the best procedure for the test to be as follows: To 5 c.c. of the aqueous solution add 15 c.c. of paraldehyde, then carefully add, with frequent shaking, just enough alcohol to make the solutions mix. Let the solutions stand over night. No advantage was found in the use of the centrifuge for collecting the precipitate. The proportion of reagents given here is the same as advocated by Amthor in the original description of the test. Amyl alcohol can be used instead of paraldehyde, as would be expected if the phenomenon were only one of lessened solubility, but offers no special advantages over the other reagent.

When the paraldehyde test was applied to vanilla extracts of known purity some difficulty was experienced. With some extracts, notably with those prepared strictly according to the United States Pharmacopœia, a gummy, brown substance was deposited on standing over night; in fact, in some cases within half an hour. This was found to be a mixture of resins and sugar, thrown out by the addition of alcohol and paraldehyde. While this precipitate did not greatly resemble caramel, it would effectually obscure it if present in slight amount.

The separation of the resins and sugar from the extract prior to making the test was a matter that caused some trouble. The resin was removed without much difficulty by evaporating the original extract to one-third its volume, making up with hot water and filtering. After numerous experiments it was found best to separate the caramel and sugar by a preliminary treatment with zinc hydroxide, as described under the phenyl-hydrazine test.

Phenyl-Hydrazine Test.—The results obtained by this test were, on the whole, better than those given by the preceding test. The solution used was a solution of two parts phenyl-hydrazine hydrochloride and three parts sodium acetate in twenty parts water. In making the test equal volumes (5 c.c.) of the reagent and the caramel solution were mixed and allowed to stand over night, the formation of a brown precipitate being noted. This test was found somewhat more delicate than the paraldehyde test, giving good results when the concentration of the caramel was reduced to 1 gram in 7,633 c.c. of water. When no caramel was present, a ring of brown flakes sometimes formed at the surface of the liquid, but these would not readily be mistaken for the caramel precipitate, which is flocculent.

It was found best in the case of extracts to concentrate the caramel by a preliminary treatment with zinc hydroxide, consisting in adding zinc chloride and potassium hydroxide to the extract, filtering the precipitate, and dissolving it in acetic acid. This solution, after being neutralized and concentrated, was found to be well adapted to either the paraldehyde or phenyl-hydrazine test. In some cases pure extracts were found to give a light gray precipitate containing zinc, but which did not resemble caramel. Fuller's earth can be used instead of the zinc hydroxide,[1] but considerable time is required to wash the earth with cold water, and on boiling with water to extract the caramel the volume of liquid is much greater than with zinc hydroxide. The zinc treatment is simpler and gives equally good results.

Use of Absorptive Reagents.—The reagent of this kind most widely used is fuller's earth, a test based on its property of removing caramel from aqueous solutions having been found to give good results in the case of spirits.[2] The test consists in adding 25 grams of fuller's earth to 50 c.c. of the suspected sample, filtering after half an hour and determining the percentage loss in color.

Quantitative tests were made of the applicability of this and other absorptive agents to vanilla extracts. The color measurements were made by means of a Duboscq colorimeter. Fuller's earth was found to remove 99 per cent. of the color when 30 c.c. of an aqueous solution of caramel of about the color of a vanilla extract were shaken with 15 grams of the earth. The percentage loss of color with a pure extract, however, under similar conditions was found to be 88 per cent. It is evident that the difference noted is much too slight to permit any point to be fixed as to just how much color an extract may give up in this manner and still be accounted a genuine product. The same objection to the fuller's earth test has been found by others in the case of vinegar.[3] Nevertheless, this method has been copied extensively and will be found given in standard works as the best method for detecting caramel in vanilla.

Basic lead acetate, as previously stated, has been recommended to remove the natural color of vanilla extract, the assumption being made that any brown or yellow color remaining is due to caramel. Quanti-

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[1] U. S. Dept. Agr., Bur. of Chem., Bull. 65, p. 71.

[2] Crampton and Simons, Jour. Am. Chem. Soc., 21, 355.

[3] W. L. Dubois, U. S. Dept. Agr., Bur. of Chem., Bull. 105, p. 23.

tative measurements showed that 95 per cent. of the natural color was removed and likewise 43 per cent. of the caramel color. It is evident that with no further criterion than the color of the filtrate the analyst would find it hard to state whether a pale yellow filtrate was due to caramel, 43 per cent. of which was retained on the filter, or whether it was the residual color from a pure, highly colored extract.

In the case of kaolin, the removal of color from caramel solutions was found to be 86 per cent.; from vanilla extracts, 76 per cent. Zinc hydroxide removed 92 per cent. from a caramel solution, and 78 per cent. from a pure extract, the difference in each case being too slight to permit the development of a satisfactory test. In brief, all of the absorptive reagents tried had appreciably similar action on caramel and vanilla, and hence have little practical value except to concentrate the caramel for some further test.

Color Quotient.—It will be remembered that no immiscible solvent was found which had any action on a caramel solution when shaken with it. It was therefore determined to endeavor to remove the natural vanilla color and leave the caramel. A number of solvents were tried successfully, ethyl acetate, amyl alcohol, and ether giving the best results. Of these, the best was probably the ethyl acetate, which removed 60 per cent. of the vanilla color and practically none of the caramel. If, now, an adulterated extract were treated with ethyl acetate, much of the natural color would be removed and but little of the caramel. A subsequent treatment with fuller's earth would give a much greater percentage loss of color than if applied to the original extract. The consideration of these facts led to the formulation of a new test for caramel, the procedure of which may be stated as follows:

A 35 c.c. sample, procured by diluting the original extract if necessary, is evaporated on the water bath to one-third its volume, to remove the alcohol and the loss made up by the addition of water. The dealcoholized extract is shaken in a separatory funnel with three successive portions of 15 c.c. each of ethyl acetate. After the last portion has been separated, part of the aqueous layer is saved for comparison and 30 c.c., or as much as possible, of the remainder is shaken with 15 grams of fuller's earth, allowed to stand for half an hour, and filtered. The percentage of color removed by ethyl acetate divided by the percentage of color removed by fuller's earth gives the "color quotient." A standard extract made according to the Pharmacopœia gave a color quotient of 2.30, whereas a caramel solution gave 0.276.

Comparison of Tests on Commercial Samples.—The method just described was compared with the other three methods on a number of pure and of adulterated vanilla extracts. For convenience the other methods are repeated here:

Paraldehyde and phenyl-hydrazine tests: 15 c.c. of the extract are mixed with 2 c.c. of zinc chloride (5 per cent. solution), and 2 c.c. of caustic potash (2 per cent. solution) are added. The precipitate is filtered, washed with hot water, and dissolved in 15 c.c. acetic acid (10 per cent. solution). This is concentrated to about half its volume, the excess of acid neutralized, and the solution divided between two test tubes. To one of these three volumes of paraldehyde are added, and just sufficient alcohol to make the mixture homogeneous. To the other tube an equal volume of a mixture of two parts phenyl-hydrazine hydrochloride, three parts sodium acetate, and twenty parts water is added. Both tubes will show a brown, flocculent precipitate after standing over night if caramel be present.

Basic lead acetate test: 10 c.c. of the extract are dealcoholized, made up to 9 c.c. with water, and 1 c.c. of basic lead acetate is added. The precipitate is filtered off and the percentage of color removed is determined.

The results of these four tests on a number of commercial extracts are given in the following table. Plus (+) signifies a positive test for caramel, minus (—) a negative test. An interrogation mark (?) indicates some slight doubt as to the result obtained. A blank space signifies that there was not a sufficient amount of the sample available to make the test.

Of these samples 1, 6, 7, and 8 were known to be pure, and 17, 24, 25, 26, 28, and 29 acknowledged on the label the presence of caramel in the extract. Judging from the results obtained on these extracts, the lead acetate method and the extraction method as used here do not give reliable results. It is quite possible that the difficulty with the lead acetate method is the small volume and slight color of the final solution. Unfortunately, where other determinations need to be made on an extract, the amount available for the caramel test is usually too small to make possible much of an increase in the volume of the filtrate from the precipitate thrown down by the basic lead acetate. From the samples known to be pure, the minimum color removed was 96.2 per cent. If it is assumed that all samples giving a color removal as large as this or larger are free from caramel, then Extract 24 would

	Paraldehyde.	Phenyl-hydrazine.	"Color quotient."	Lead acetate.
				Per cent. color removed.
1	—	—	2.26	96.2
2	—	—	0.345	98.7
3	—	—	0.175	95.1
4	—	—	1.28	91.8
5	—	—	0.679	97.9
6	—?	—	1.86	99.2
7	—	—	1.04	88.3
8	—	—	0.934	97.5
9	—	—	1.49	99.0
10	—	—	0.322	97.0
11	—	—	2.06	98.2
12	—	—	1.62	96.8
13	—	—	1.24	. .
14	—	—	0.167	97.7
15	—?	—	. .	98.3
16	—	—	. .	97.1
17	. .	. .	1.21	95.8
18	+?	. .	1.74	96.2
19	+	+	0.799	97.6
20	—?	+	0.0	98.4
21	+	—	1.35	98.0
22	+	—	1.06	99.2
23	+	+	0.462	99.2
24	+	+	0.547	97.1
25	+	+	0.137	96.7
26	+	+	1.03	95.4
27	+	+	0.651	96.4
28	+	+	0.564	93.6
29	+	+	0.598	91.0
30	+	+	0.706	94.1
31	+	+	0.274	88.7
32	+	+	0.232	84.9
33	+	+	0.483	. .

be declared satisfactory, whereas it is admitted to contain caramel, and the other tests substantiate this statement. Many of the unknown samples, as well, show caramel by the other tests, but not by this one.

A consideration of the color quotients obtained with the extraction and absorption method shows this to be open to the same criticism as the basic lead acetate method. The minimum value obtained with the pure extracts is .934, whereas two of the adulterated extracts give quotients of 1.21 and 1.03, and so no figure can be established as the dividing line between pure extracts and extracts containing caramel.

The paraldehyde and phenyl-hydrazine tests as used here give results that agree with the facts of the case, and in the few instances where the result of one method is doubtful the accompanying test by the other method is sufficient to remove the doubt. The amount of sample required is only 15 c.c. and the use of a colorimeter is not necessary.

The procedure found to give the best results in this investigation and recommended for use is as follows: 15 c.c. of the extract are mixed with 2 c.c. of zinc chloride (5 per cent. solution), and 2 c.c. of caustic potash (2 per cent. solution) are added. The precipitate is filtered, washed with hot water, and dissolved in 15 c.c. of acetic acid (10 per cent. solution). This is concentrated to about half its volume, the excess acid neutralized, and the solution divided between two test tubes. To one of these three volumes of paraldehyde are added and just sufficient alcohol to make the mixture homogeneous. To the other tube an equal volume of a mixture of two parts phenyl-hydrazine hydrochloride, three parts sodium acetate, and twenty parts water is added. Both tubes will show a brown, flocculent precipitate after standing over night if caramel be present.

CONTRIBUTIONS FROM THE
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No. 37

DETERMINATION OF THE HYDRATION OF IONS BY TRANSFERENCE EXPERIMENTS IN THE PRESENCE OF A NONELECTROLYTE[1]

BY EDWARD W. WASHBURN

I. PRINCIPLE OF THE METHOD

IF the transfer of electrolyte from one electrode to the other during a transference experiment is accompanied by a transfer of water, as would be the case if the ions are hydrated and carry water with them as they move through the solution, it is evidently possible to detect this transfer of water by having present in the solution a third constituent, which remains stationary during the passage of the current. By referring changes in content both of water and of electrolyte to this "reference-substance," the amounts of each transferred can be determined; and from these the "true"[2] transference numbers (T_t) can be calculated, and information in regard to the hydration of the ions derived.

II. REVIEW OF PREVIOUS INVESTIGATIONS

The first attempt to apply this principle was made by Nernst and his students.[3] In their experiments solutions of sulphuric, hydrochloric, hydrobromic, and nitric acids, containing boric acid as the reference-substance, were electrolyzed between platinum electrodes. The elec-

[1] This investigation was carried out with the aid of a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington.

[2] In the usual method of calculating transference numbers the assumption is made that the solvent is absolutely stationary; that is, that no transfer of solvent takes place from one electrode to the other. If such a transfer of solvent takes place, the calculation of the transference number by the ordinary method is not justified and will not give the *true transference number*, T_t. In fact, the number so obtained does not represent any physical quantity. Only in dilute solutions, where the amount of solvent transferred becomes negligible in comparison with the total solvent present, will the ordinary transference number, T_o, approach the true one, T_t.

[3] Nernst, Gerrard, and Oppermann, Nachr. Gesells. Wissensch., Göttingen, 56, 86 (1900).

trode at which the concentration of the electrolyte increased was contained in a pipette placed in a beaker filled with the solution. The strong acid was determined by titration with 0.05 normal baryta solution, using methyl orange; and the boric acid, after the addition of mannite, was titrated similarly, using phenol phthalein. The errors involved in the analytical methods, amounting to from 0.2 to 0.3 per cent., render it impossible to draw any definite conclusion from their results, except that if water is transported at all under these conditions the amount is not very large.

Two years later Lobry de Bruyn[1] took up the problem. In his experiments a solution of silver nitrate containing methyl alcohol as the reference-substance was electrolyzed between silver electrodes in the "ordinary transference apparatus." The content in silver nitrate was determined by titration, and that in methyl alcohol by the distillation method. The author concludes that, "On peut facilement calculer que si l'ion Ag (ou l'ion NO_3) devait transporter, par example, une molécule du dissolvant, on trouverait pour une quantité de 4 grammes Ag à l'anode ou à la cathode respectivement une augmentation et une diminution, en eau de 0.6 à 0.7 gramme, ou en alcool méthylique de ± 1.2 grammes. L'analyse aurait montré qu'il en était ainsi, même si par diffusion les quantités avaient diminuées . . . ; il est donc à propos d'admettre que les ions . . . n'emportent pas le dissolvant avec eux, mais se meuvent seuls et libres." An examination of the experimental data does not justify this conclusion. Owing to the change in the boiling point of the solution with varying content of silver nitrate, the above mentioned change in composition might easily have escaped detection by the distillation method of analysis. Furthermore, the use of methyl alcohol as a reference-substance, especially in the high concentrations used by de Bruyn (24 to 64 per cent.), is open to grave objections, as will be explained below.

These two investigations constituted the only attempts which had been made to apply the method up to the time of the commencement of the present investigation.[2] During the progress of this investigation

[1] Lobry de Bruyn, Rec. trav. chim., 22, 430 (1903).

[2] This investigation was begun in the latter part of 1904. In the earlier part of the investigation a molal sodium chloride solution was studied, using sugar (0.3 molal) as the reference-substance. The results of this part of the investigation, in which it was definitely shown that water was transported from anode to cathode during the electrolysis, were presented at a meeting of the Harvard-Technology Physico-Chemical Club, in May, 1905, and are recorded in the author's thesis of that year. (Mass. Inst. Tech., Chemical Theses, 1905.)

two other contributions to the problem have appeared. Morgan and Kanolt [1] attacked the problem, using solutions of silver nitrate in mixtures of alcohol and water. The analytical method for estimation of the alcohol content of the solutions before and after the electrolysis was considerably improved over the one used by de Bruyn, and every precaution was taken to prevent evaporation of the alcohol. As the experiments were intended to be qualitative only, the form of the apparatus was not adapted to quantitative experiments, since no middle portion was taken; and the electrolysis was prolonged, so that mixing of the electrode portions undoubtedly took place to some extent. The authors reasoned that "the best conditions for the detection of the combination of the water with the ions are found in a solution containing much less water than alcohol"; consequently they used solutions containing 53 per cent. and 66 per cent., respectively, of alcohol. Such a procedure is open, however, to serious objections. There is reason to believe [2] that in alcoholic solutions combination between this solvent and the ions also takes place, and if such is the case, the use of high concentrations of alcohol simply serves to complicate the problem. In fact, one essential condition should be that the concentration of the reference-substance in the solution be so small that its active mass shall be negligible in comparison with that of the solvent. Morgan and Kanolt were able to detect a change in the ratio of water to alcohol only in the 66 per cent. alcohol solution. In this case the change, while small, was probably outside the errors of experiment, and indicated that water was carried by the silver-ion or alcohol by the nitrate-ion, two possibilities of equal *a priori* probability between which it is impossible to distinguish.

The results of the three investigations just described left the question of hydration still an open one. To Gustav Buchböck [3] we owe the first successful application of the principle of this method. Working with solutions of hydrochloric acid and using mannite and resorcin at small concentrations as the reference-substances, he was able to prove that water is transported from the anode to the cathode during the electrolysis of these solutions. A satisfactory measurement of the amount transported was also obtained, the results at the two elec-

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[1] Morgan and Kanolt, J. Am. Chem. Soc., 28, 572 (1906).

[2] See Carrara, Ahrens' Sammlung, 12, 413 (1908).

[3] Buchböck, Z. physik. Chem., 55, 563 (1906).

trodes checking very well with each other. The results obtained with the two reference-substances are also nearly identical within the experimental error. His apparatus is shown in Figure 1. The two halves were connected by a ground glass joint at *b*, and the two stopcocks, *e* and *f*, permitted the separation of the solution into three parts at the completion of the electrolysis. The cathode was a small platinum wire sealed into the apparatus, and the anode (shown in cross-section) a torus made of the finest silver gauze. These two electrodes were enclosed between the wall and the short insert tubes, as shown. A diaphragm of silk gauze over the bottom of the insert tube on the cathode

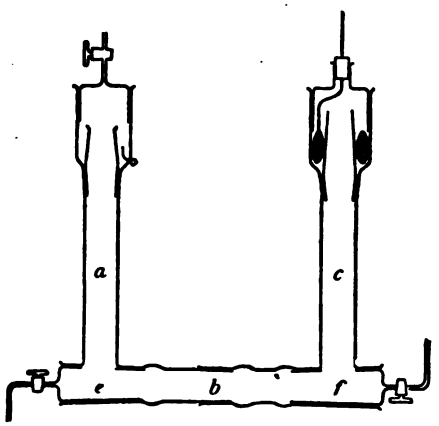

FIG. 1

side served to restrict the stirring caused by the evolution of hydrogen at this electrode.

The concentration of the hydrochloric acid was determined with an accuracy of a few hundredths of 1 per cent. by titration with an alkali solution free from carbonate in a weight burette, using phenol phthalein as the indicator. To determine the mannite, the solution, after neutralization with pure silver carbonate and removal of the excess of silver with hydrogen sulphide, was evaporated to dryness in a platinum dish and the mannite weighed directly. An accuracy of 0.05 to 0.10 per cent. was attained. In the experiments with resorcin as the reference-substance the content was determined by extracting the solution ten times with ether, evaporating the ethereal solution in a specially constructed apparatus, drying the residue in a current of hydrogen, and

weighing it directly. The accuracy was probably not better than 0.1 per cent.

In order to show that the reference-substance did not of itself migrate with the current, a regular transference experiment was made with a pure mannite solution in which 110 volts were applied to the electrodes for ten and a half hours. The silver coulometer showed a deposit of 0.004 gram of silver, and the analyses did not indicate any tendency on the part of the mannite to migrate with the current. The experimental data of Buchböck will be given and discussed later in connection with the results of the present investigation.

III. The Reference-Substance

The plan of the present investigation was to find a suitable material to use as a reference-substance, and then to measure the true transference numbers of the chlorides of the alkali metals and the quantity of water simultaneously transferred. Since the success or failure of this method depends almost entirely upon the properties of the reference-substance, this phase of the problem will first be discussed.

A satisfactory reference-substance must possess all of the following properties:

1. It must be a nonelectrolyte and must remain stationary with respect to the water when a current of electricity is passed through a solution containing it. This excludes all substances of a colloidal nature.

2. It must be a stable substance and must not react with or be acted upon by the electrodes, the solvent, the electrolyte, or any substance formed during the electrolysis.

3. Since the object of the investigation is to obtain information in regard to the state of hydration of the ions in *aqueous* solution, it is obvious that the reference-substance must be present at such a small concentration that it shall not appreciably change the character of the solvent.

4. Since, moreover, the changes in the ratio of water to reference-substance at the electrodes will be small, the reference-substance must be capable of very accurate estimation.

Since nearly all of the substances which fulfill the first of these conditions are organic compounds, and since such compounds do not fulfill the second condition in solutions of the alkali chlorides when they are electrolyzed between platinum electrodes, it became necessary,

first of all, to devise electrodes which could be used in these solutions without the appearance of oxygen or hydrogen, or the formation of acid or alkali, during the electrolysis. To meet this requirement the apparatus and electrodes described in a previous communication[1] were devised, and were used throughout this investigation. The silver anode and the silver chloride cathode prevented entirely the evolution of any gas or the formation of acid or alkali, and they had the further advantage of not introducing any foreign substance into the solution.

In choosing a reference-substance no compound was considered available unless its concentration in a 0.1 to 0.3 molal solution could be determined to 0.01 per cent. Three substances were found which fulfilled this condition, sucrose, raffinose, and arsenious acid. The final test of the availability of a compound for use as a reference-substance is its ability to remain entirely unchanged in the solution during an electrolysis with a current of 0.1 ampere for a period of at least fifteen hours. This final test is applied by making what is called a "straight tube run." This run differs in no way from the regular transference runs, except that it is made in a straight tube, with the silver anode at the top and the silver chloride cathode at the bottom. At the end of the run, instead of separating the solution into several portions, it is thoroughly mixed without opening the apparatus, and after the silver chloride has settled a portion of the solution is removed with a pipette and analyzed for the reference-substance. The substance is considered to be satisfactory if its concentration is the same (to 0.01 per cent.) at the end of this test as it was in the original solution. When the three substances mentioned above were subjected to this test only one of them, raffinose, was found to fulfill this condition rigorously. The results obtained with the other two are, therefore, only approximate. They will, however, be described, since they furnish checks on the order of magnitude and direction of transport of the water.

IV. Purification of Material

Sucrose. — The sucrose employed was a special unblued product, obtained directly from the refinery. It was further purified by three precipitations from water solution by the addition of pure alcohol. After washing with pure alcohol and ether, the crystals were dried at

[1] This Quarterly, 21, 164 (1908).

95° and kept over calcium chloride. It had a specific rotatory power in 9.43 per cent. solution of $[\alpha]_D^{25°} = 66.410° \pm 0.0038$, and the specific conductance of the solution was less than 3.10^{-6} reciprocal ohms.

Raffinose. — This material was obtained from Kahlbaum, and was further purified by several recrystallizations from hot, pure methyl alcohol. The viscous mass which resulted from these crystallizations was dissolved in water and thrown out by diluting with pure ethyl alcohol. The beautifully crystalline product thus obtained was washed with alcohol and ether and dried at 50°.

Sodium Chloride. — This salt was prepared from Kahlbaum's product by precipitation with hydrochloric acid gas. After washing and drying, the salt was fused in platinum to ensure the removal of the last traces of hydrochloric acid.

Potassium Chloride. — Kahlbaum's product was recrystallized four times from conductivity water and the crystals fused in platinum. The salt gave a pure potassium flame.

Lithium Chloride. — Pure lithium carbonate was prepared from the commercial article by eight precipitations of the nitrate solution with pure ammonium carbonate, according to the method of Stas.[1] The resulting product was heated to 600° in an electric oven to remove ammonium salts. A solution of hydrochloric acid was prepared by expelling the gas from pure HCl solution (sp. gr. 1.20) with H_2SO_4 and receiving it in conductivity water. This solution was saturated with the lithium carbonate, and after filtering the filtrate was acidified with an excess of hydrochloric acid and evaporated to dryness. The lithium chloride thus obtained was dissolved to form a 1.3 molal solution. In order to make sure that the solution was exactly neutral it was tested with phenol phthalein, rosolic acid, and congo red, according to the method of Salm;[2] and the hydrogen-ion concentration was found to lie between the values 10^{-6} and 10^{-8}. The solution was consequently neutral, and it was used in preparing the solution for the lithium chloride experiments.

Arsenic Trioxide. — Kahlbaum's preparation was once resublimed and then twice recrystallized from hot water.

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[1] Stas, Ouvres I, 689.

[2] Salm, Z. physik. Chem., 57, 500 (1907).

V. Preparation of Solutions

All the water used in preparing the solutions was conductivity water from the special still in this laboratory.[1] The raffinose and sugar solutions were prepared on the same day that the transference experiment was made, and were filtered through hardened filters to ensure the absolute clarity which is necessary for accurate polariscopic work. Just previous to filling the apparatus with the solution all dissolved oxygen was removed by boiling for five minutes at 30° under reduced pressure. All solutions were cooled to 2° above the dew-point whenever the transference of the solution from one vessel to another involved a possibility of a change in concentration due to evaporation.

In preparing the arsenious acid solutions, arsenic trioxide was dissolved in hot conductivity water and, after dilution to the proper concentration, the sodium chloride was added, and the whole solution was rotated for twenty-four hours at 25° in contact with a mixture of silver chloride and silver[2] to ensure equilibrium. Dissolved oxygen was removed by evacuation, and the solution was ready for use.

VI. Analytical Methods

Sucrose and Raffinose. — The concentrations of these two substances were determined by the optical method. This method, which is capable of a high degree of accuracy, has the further advantage that the whole of the electrode portion can also be used for the determination of the electrolyte, since the estimation of the carbohydrate does not affect the solution in any way when precautions are taken to prevent evaporation.

The polariscope used was a Schmidt and Haensch half-shade instrument of the Lippich type, the scale reading directly to tenths of a degree and the vernier directly to thousandths. The light was furnished by igniting sticks of fused sodium carbonate in an oxyhydrogen flame, and was further purified by filtration through a Landolt-Lippich ray filter. The instrument was kept in a dark room of even temperature, and was connected with a thermostat maintained at 25°, from which water was caused to circulate around the jacket of the 60-cm. polarizing tube. The average deviation of a set of six readings on this

[1] See Noyes and Coolidge, Proc. Am. Acad., 39, 190 (1903); Carnegie Inst. Pub., No. 63, 39 (1907).

[2] Such a mixture as is obtained from the cathode after a transference experiment.

instrument amounted to only 0.003° for a total rotation of 30°, thus permitting an accuracy of 0.01 per cent. in the reading. The same 60-cm. tube was used throughout this investigation. It was jacketed with a nickel-plated water jacket, and was provided with a thermometer in the side tube.

For the determination of the specific gravity of the solutions, pycnometers of the Ostwald-Sprengel type, having a capacity of 20 c.c.

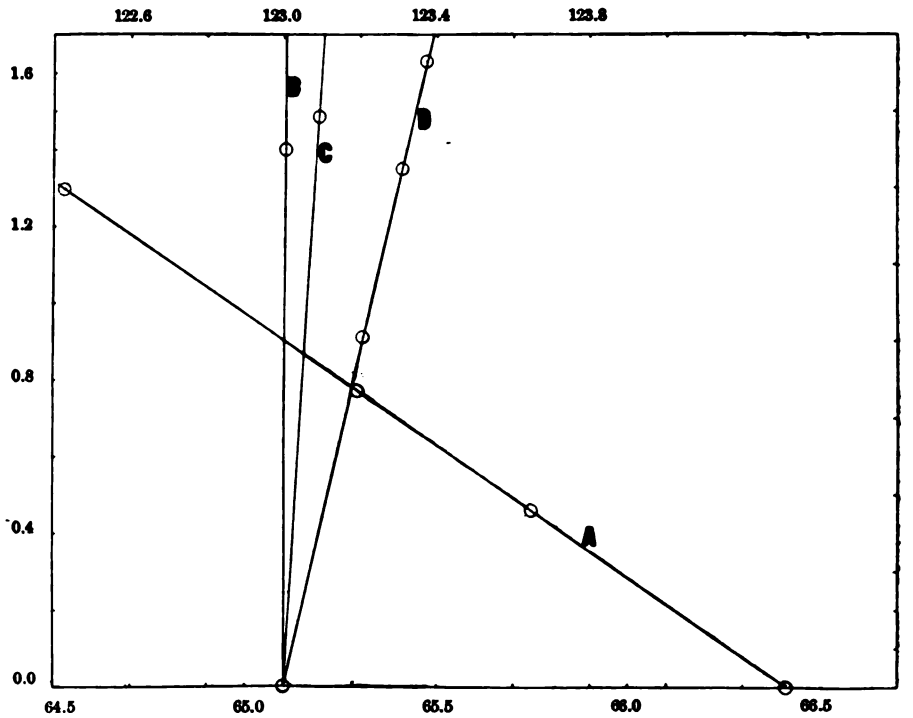

FIG. 2

and provided with ground glass caps, were used. (All specific gravities are at 25°, referred to water at 4°.) Air-free conductivity water was used in obtaining the water value of the pycnometer. A second pycnometer of the same type was used as a counterpoise, and all weights were reduced to vacuo. The error in the specific gravity determination never amounted to 0.01 per cent.

Effect of Salts on the Specific Rotatory Power. — Sodium chloride is known to reduce the specific rotatory power of cane sugar solutions,

the lowering depending upon the initial concentration of the sugar and being proportional to the amount of salt added.[1] It became necessary, therefore, to make a careful determination of this effect, so that corresponding corrections could be applied without introducing too large an error. The result of these determinations is shown in Figure 2, curve *A*. In this figure values of $[\alpha]_D^{25°}$ are plotted as abscissæ (on lower line) and values of $\frac{P_s}{P_r}$ as ordinates, P_s representing the per cent. of salt (in this case NaCl) and P_r the per cent. of sugar in the solution, the ratio of sugar to water, $\frac{P_r}{P_w}$, being kept constant and in this case equal to 9.60. As is evident from this figure, the graph obtained is a perfectly straight line; its position, however, varies according to the ratio of sugar to water in the solution.

The effects of KCl, NaCl, and LiCl upon the specific rotatory power of raffinose were also investigated. A solution of raffinose, containing 0.1 formula-weight ($C_{18}H_{32}O_{16}$) per 1,000 grams of water, was employed. The results are given in the following table:

Salt.	Molal conc. of salt.	$[\alpha]_D^{25°}$.
. . . . .	0.0	123.00°
KCl	1.3	123.08°
NaCl	1.71	123.12°
LiCl	1.30	123.24°

It is to be noted that the presence of the salts produces an increase in the specific rotatory power instead of a decrease, as in the case of sugar. The effect of LiCl was determined at three different concentrations and found to be linear. In none of the solutions, however, was it found necessary to apply any correction to the specific rotatory power of the raffinose due to the changes in the salt concentration at the electrodes, the correction being entirely negligible. Raffinose seems to possess the properties of an ideal reference-substance, being very

[1] See Muntz, Z. Ver. Zuckerind, 26, 376 (1876), and Farnsteiner, Z. Ver. Zuckerind, 41, 168 (1891).

stable in the apparatus and having a high specific rotatory power, which is not appreciably affected by changes in temperature or by changes in the concentration of the raffinose itself or of salts in the solution. The curves, showing the effects of these salts upon the specific rotatory power of raffinose, are also given in Figure 2. Curve *B* is for KCl, *C* for NaCl, and *D* for LiCl. Values of $[\alpha]_D^{25°}$ are plotted as abscissæ (upper line) and values of $\frac{P_s}{P_r}$ as ordinates.

Arsenious Acid. — This substance was estimated by titration with standard iodine solution, using disodium phosphate as the neutralizing agent. The details of this method, when an accuracy of 0.002 per cent. is required, have been described by the author in a previous paper.[1]

The Salts. — The chloride in the solution was determined by precipitating it from a weighed amount of the solution by means of an excess of a pure silver nitrate solution, and collecting and weighing the precipitate on a platinum Gooch crucible. The procedure was substantially that followed by Richards and Wells[2] in their "Revision of the Atomic Weights of Sodium and Chlorine." An accuracy of 0.01 per cent. was attained. The weights used in this investigation were carefully calibrated, and all weighings have been reduced to vacuo.

VII. Notation

$\alpha^{25°}$,	angular rotation of the plane of polarization by the solution at 25°.
$d^{25°}/_{4°}$,	specific gravity of the solution at 25° referred to water at 4°.
P_r,	per cent. of the reference-substance in the solution.
P_s,	per cent. of the electrolyte in the solution.
Ag^c,	grams of silver deposited in the coulometers.
m^c,	total mass in grams of the electrode portion.
Δm_w, Δn_w	increase in grams (resp. mols) of water in the electrode portion.
Δm_s, Δn_s	increase in grams (resp. mols) of electrolyte in the electrode portion.
$\mathcal{N}$,	equivalents of electricity passed through the solution.
T_t^c, T_t^a,	true transference number of the cation (resp. anion).
T_o^c, T_o^a,	ordinary transference number of the cation (resp. anion).

[1] J. Am. Chem. Soc., 30, 31 (1908).

[2] Richards and Wells, Carnegie Inst. Pub., No. 28.

Δn_w^F, number of mols of water transferred from anode to cathode per faraday of electricity.

A, anode portion.

M_A, M, M_c, anode-middle, resp. middle, resp. cathode-middle portion.

C, cathode portion.

The most rational quantity to use in comparing the results at the two electrodes is the ratio of water transferred to salt transferred, *i. e.*, $\frac{\Delta n_w}{\Delta n_s}$, since this quantity depends only upon the analyses and is independent of the total weight of the electrode portion. This quantity will accordingly be inserted in the tables.

The final results of each experiment are most conveniently expressed by an equation which will be written in the two forms, A and B.

$$T_t^c N_w^c - T_t^a N_w^a = \Delta n_w^F. \qquad (A)$$

$$N_w^c = \frac{\Delta n_w^F}{T_t^c} + \frac{T_t^a}{T_t^c} N_w^a. \qquad (B)$$

In these equations N_w^c and N_w^a are the number of water molecules combined with one cation and one anion, respectively. The product of each of these quantities by the corresponding transference number is evidently the total amount of water carried by each ion when one equivalent of electricity passes through the solution, and the difference between these quantities represents the number of mols of water transferred from anode to cathode per faraday equivalent. Form B expresses the number of water molecules combined with the cation as an explicit function of the number combined with the anion. In this equation the constant, $\frac{\Delta n_w^F}{T_t^c}$, is evidently identical with the quantity, $\frac{\Delta n_w}{\Delta n_s}$. In using these general equations in the following sections, the superscripts, *c* and *a*, will be replaced by the symbol of the element in question in each case.

VIII. Data and Results with Sodium Chloride

Reference-Substance — Raffinose

Composition of solution:

Sodium chloride, 1.21 formula-weights of NaCl per 1,000 grams of water.

Raffinose, 0.1 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.

Applied E.M.F., 19 volts.
Current, 0.075 ampere
Duration of run, 12 hours.

TABLE I

	A.	M_A.	*M.*	M_c.	C.
$\alpha^{25°}$	34.90°	34.32°	34.33°	34.31°	33.80°
$d^{25°}/_{4°}$	1.0495	. .	1.0608	. .	1.0705
P_r	4.584	. .	4.449	. .	4.341
P_s	4.731	. .	6.344	6.343	7.702
Ag^c	6.788	. .	. .	. .	6.787
m^c	78.13	. .	. .	. .	. .
Δm_w	—0.96	. .	. .	. .	. .
Δn_w	—0.53	. .	. .	. .	. .
Δm_s	—1.41	. .	. .	. .	. .
Δn_s	—0.0241	. .	. .	. .	. .
$\mathcal{N}$	—0.0629	. .	. .	. .	. .
$T_i^c = \frac{\Delta n_s}{\mathcal{N}}$	0.383	. .	. .	. .	. .
T_i^a	0.617	. .	. .	. .	. .
T_o^c	0.366	. .	. .	. .	.
T_o^a	0.634	. .	. .	. .	.
$\frac{\Delta n_w}{\Delta n_s}$	2.2	. .	. .	. .	2.0
n_w^F	0.84	. .	. .	. .	0.78

The data and results are shown in Table I. Owing to an uncertainty in the total weight of the cathode portion in this experiment, the transference number could not be obtained from this portion. The ratio of water to salt transferred, $\frac{\Delta n_w}{\Delta n_s}$, however, checks with the value obtained from the anode portion.

Reference-Substance — Sucrose

Several experiments were made with sodium chloride solutions, using sucrose as the reference-substance. In every case an increase in the concentration of the sugar at the anode and a corresponding decrease at the cathode were observed. Owing, however, to the uncertain stability of the sugar under the action of the electrode processes, the results were not very accurate from the quantitative standpoint. The best of these runs, with a 0.3-molal sugar solution, gave a value of the ratio, $\frac{\Delta n_w}{\Delta n_s} = 2$, at the anode and $\frac{\Delta n_w}{\Delta n_s} = 4$ at the cathode.

The low value of the conductivity of a pure sugar solution indicates the absence of any tendency on the part of the sugar to migrate under the influence of the E.M.F. However, in order to make sure that the presence of the sodium chloride is necessary in order to produce a concentration change at the electrodes when an electromotive force is applied for several hours to a sugar solution, the following experiment was made. A 10 per cent. sugar solution, containing 0.008 per cent. of sodium chloride, was placed in the regular transference apparatus, and a potential of 231 volts applied at the electrodes for the same length of time as in the regular transference runs. At the end of this time the solution in the neighborhood of each electrode was polarized, and the result was found to be identical with that given by the middle portion and by the original solution. It is thus evident that no concentration change takes place at the electrodes in the absence of the electrolyte, even with an electromotive force twelve times as great as in the regular runs.

Reference-Substance — Arsenious Acid

Arsenious acid did not prove to be a satisfactory reference-substance, owing to its uncertain stability during the passage of the current. One run, however, was obtained in which the arsenious acid had apparently undergone no oxidation at the electrodes, since the total amount present in the two electrode portions was equal to the amount present in the same weight of original solution. An increase of concentration was observed at the anode and a corresponding decrease at the cathode. The results are shown in the following table.

Composition of the solution:
Sodium chloride, 1.25 formula-weights of NaCl per 1,000 grams of water.
Arsenious acid, 0.20 formula-weight of H_3AsO_3 per 1,000 grams of water.

TABLE II

	Anode.	Cathode.
Δc	4.245	4.246
Δm_w	—0.35	0.36
Δn_w	—0.019	0.020
Δn_s	—0.0147	0.0149
N	0.0393	0.0393
$T_s = \frac{\Delta n_s}{N}$	0.374	0.379
$\frac{\Delta n_w}{\Delta n_s}$	1.3	1.3

Numerous attempts were made to repeat the results with arsenious acid, but without success, as check results at the two electrodes could not be obtained. A "straight tube run" showed a loss of arsenious acid, apparently due to oxidation. In view of this fact, the quantitative agreement of the results at the two electrodes, as shown in the above table, is to be regarded as more or less accidental, and the results are, therefore, chiefly of value as showing a concentration change in the same direction and of the same order of magnitude as in the case of sugar and raffinose.

Summary of the Results with Sodium Chloride

Three solutions of sodium chloride (1.2 molal), containing, respectively, as reference-substances, raffinose, sucrose, and arsenious acid, each at low concentration, were electrolyzed between reversible electrodes. In each case an increase in the concentration of the reference-substance was observed at the anode and a corresponding decrease at the cathode. If the assumption be made that the change in concentration is due to the transfer of water from anode to cathode during the electrolysis, the three experiments agree in showing that the ratio of mols of water

transported to mols of salt transported, $\frac{\Delta n_w}{\Delta n_s}$, lies between the values 1 and 4. The value obtained with raffinose is to be regarded as the most reliable value. The final values adopted for NaCl are given by the following equations:

$$0.383\, N_w^{Na^+} - 0.617\, N_w^{Cl^-} = 0.76 \pm 0.08,$$

$$\text{or} \quad N_w^{Na^+} = 2.0 \pm 0.2 + 1.61\, N_w^{Cl^-}.$$

IX. Data and Results with Potassium Chloride

Reference-Substance — Raffinose

Composition of solution:

Potassium chloride, 1.24 formula-weights of KCl per 1,000 grams of water.

Raffinose, 0.1 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.

Applied E.M.F., 19 volts.

Current, 0.096 ampere.

Duration of run, 14 hours.

	$C_{18}H_{32}O_{16}$	KCl
Total amount of solute in anode and cathode portions at completion of the run,	8.32 grams	15.27 grams
Total amount of solute in same weight of original solution,	8.33 grams	15.27 grams

The results are shown in Table III.

TABLE III

	A.	M_A.	*M.*	M_c.	*C.*
$\alpha^{25°}$	35.262°	34.827°	34.824°	34.825°	34.213°
$d^{25°}/_{4°}$	1.0578	1.0681	1.0681	. .	1.0807
P_r	4.516	. .	4.418	. .	4.290
P_s	6.510	8.105	8.108	8.108	10.030
Ag^c	5.3685	. .	. .	. .	5.3681
m^c	103.21	. .	. .	. .	85.280
Δm_w	—0.47	. .	. .	. .	0.61
Δn_w	—0.026	. .	. .	. .	0.034
Δm_s	—1.836	. .	. .	. .	1.839
Δn_s	—0.02460	. .	. .	. .	0.02465
$\mathcal{N}$	0.04974	. .	. .	. .	0.04974
$T_t^c = \frac{\Delta n_s}{\mathcal{N}}$	0.495	. .	. .	. .	0.495
T_t^a	0.505	. .	. .	. .	0.505
T_o^c	0.483	. .	. .	. .	0.481
T_o^a	0.517	. .	. .	. .	0.519
$\frac{\Delta n_w}{\Delta n_s}$	1.1	. .	. .	. .	1.4
n_w^F	0.52	. .	. .	. .	0.68

Summary of Results with Potassium Chloride

The direction of the concentration change is the same as with sodium chloride, but the amount of water transported is less. An especially noteworthy result is the value, 0.495, of the true transference number for the cation. *This is identical with the value obtained by Jahn,*[1] *at 25°, for KCl at infinite dilution, showing that the transference number for KCl is independent of the concentration up to 1.2 molal at least.* The value of the ordinary transference number at this concentration is 0.482, which illustrates the error introduced in transference

[1] Jahn, Z. physik. Chem., 58, 645 (1907).

work if hydration is neglected. The final values adopted for KCl are shown in the following equations:[1]

$$0.495\, N_w^{K^+} - 0.505\, N_w^{Cl^-} = 0.60 \pm 0.08, \qquad \text{(A)}$$

$$\text{or} \quad N_w^{K^+} = (1.3 \pm 0.2) + 1.02\, N_w^{Cl^-}. \qquad \text{(B)}$$

X. Data and Results with Lithium Chloride

Reference-Substance — Raffinose

Composition of solution:

Lithium chloride, 1.28 formula-weights of LiCl per 1,000 grams of water.

Raffinose, 0.104 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.

Applied E.M.F., 19 volts.

Current, 0.096 ampere.

Duration of run, 13 hours.

	$C_{18}H_{32}O_{16}$	LiCl
Total amount of solute in anode and cathode portions at the completion of the run,	8.78 grams	9.17 grams
Total amount of solute in same weight of original solution,	8.79 grams	9.18 grams

The results are shown in Table IV.

[1] In addition to the run with KCl and raffinose, a run with KCl and sucrose was also made, and an increase in the sucrose concentration at the anode and a corresponding decrease at the cathode were observed. The analyses were not completed, however, as quantitative results could not have been obtained without a careful investigation of the change in specific rotatory power of the sucrose, with varying concentrations of potassium chloride, and such an investigation did not seem worth while in view of the uncertain stability of the sugar during the electrolysis.

TABLE IV

	A.	M_A.	*M.*	M_c.	C.
$\alpha^{25°}$	37.045°	36.540°	36.558°	36.557°	35.819°
$d^{25°}/4°$	1.0427	1.0454	1.0452	. .	1.0484
P_r	4.806	. .	4.730	. .	4.619
P_s	4.440	4.938	4.939	4.943	5.565
Ag^c	5.0116	. .	. .	. .	5.0112
m^c	104.4	. .	. .	. .	81.47
Δm_w	—1.1	. .	. .	. .	1.3
Δn_w	—0.62	. .	. .	. .	0.070
Δm_s	—0.604	. .	. .	. .	0.594
Δn_s	—0.0142	. .	. .	. .	0.0140
$\mathcal{N}$	0.04643	. .	. .	. .	0.04643
$T_t^c = \frac{\Delta n_s}{\mathcal{N}}$	0.306	. .	. .	. .	0.301
T_t^a	0.694	. .	. .	. .	0.699
T_o^c	0.278	. .	. .	. .	0.273
T_o^a	0.722	. .	. .	. .	0.727
$\frac{\Delta n_w}{\Delta n_s}$	4.3	. .	. .	. .	5.1
n_w^E	1.4	. .	. .	. .	1.6

Summary of the Results with Lithium Chloride

The concentration change is in the same direction as in the case of NaCl and KCl, but the amount of water transported is larger than with either of the other salts. The final values adopted for LiCl are shown by the following equations:

$$0.302\, N_w^{Li^+} - 0.698\, N_w^{Cl^-} = (1.5 \pm 0.1), \qquad \text{(A)}$$

$$\text{or} \quad N_w^{Li^+} = (4.7 \pm 0.4) + 2.29\, N_w^{Cl^-}. \qquad \text{(B)}$$

XI. Results with Hydrogen Chloride

TABLE V

Conc. reference-substance.	Conc. HCl.	T_t^c.			$\frac{\Delta n_w}{\Delta n_s}$.		
		Anode.	Cathode.	Mean.	Anode.	Cathode.	Mean.
Reference-Substance — Mannite							
0.135	1.0	0.844	0.844	0.844	0.30	0.28	0.29 ± 0.01
0.297	1.0	0.845	0.845	0.845	0.21	0.28	0.25 ± 0.03
0.141	1.47	0.836	0.840	0.838	0.33	0.34	0.33 ± 0.01
0.353	1.47	0.844	0.844	0.844	0.25	0.24	0.24 ± 0.02
0.353	1.47	0.843	0.844	0.844	0.22	0.26	
0.717	1.47	0.845	0.847	0.846	0.21	0.23	0.22 ± 0.01
Reference-Substance — Resorcin							
0.214	1.1	0.840	0.842	0.841	0.29	0.39	0.34 ± 0.05
0.408	1.1	0.843	0.842	0.842	0.38	0.34	0.36 ± 0.02
1.07	1.1	0.845	0.844	0.845	0.46	0.39	0.42
1.98	1.1	0.845	0.844	0.844	0.49	0.41	0.45
0.328	3.07	0.839	0.840	0.840	0.40	0.41	0.41
0.636	3.07	0.837	0.838	0.837	0.43	0.39	0.41
1.31	3.07	0.839	0.838	0.839	0.47	0.47	0.47

The results obtained by Buchböck have been recalculated so as to show the values of $\frac{\Delta n_w}{\Delta n_s}$ and of T_t^c, obtained at each electrode.[1] These values are shown in Table V, concentrations being expressed in formula-weights per 1,000 grams of water. The excellent agreement of the results at the two electrodes attests the high degree of accuracy which

[1] Buchböck apparently did not make use of the total number of equivalents of electricity passed through the solution, as shown by his coulometer. The values of T_t given by him are, therefore, the means of the two values which can be obtained from each electrode separately. He gives, also, only the change in the number of *grams* of water at each electrode, a quantity which is dependent upon the total weight of the electrode portion and which is more liable to be affected by any error arising from admixture with the middle portion than is the value of $\frac{\Delta n_w}{\Delta n_s}$. I have accordingly computed values of T_t^c and of $\frac{\Delta n_w}{\Delta n_s}$ for each electrode from his original data.

this investigator was able to attain in his analyses. In fact, only two criticisms of the experimental part of the work can be made: (1) the failure to maintain a constant temperature by use of a thermostat, and (2) the analysis of only one middle portion. In regard to the first of these, the author does not record the temperature at which his experiments were carried out, but simply makes the statement: "Ein grosser Teil der Unsicherheiten . . . mag übrigens darauf zurückzuführen sein, dass die Temperatur bei diesen Versuchen nicht berücksichtigt wurde, . . . so kann zwischen einzeln, differenz von etwa 10° bestanden haben, was auf die Resultäte nicht einflusslos geblieben sein durfte." The necessity for analyzing more than one middle portion in transference work has already been discussed.[1]

An examination of the results obtained with mannite leads to the conclusion that the value of $\frac{\Delta n_w}{\Delta n_s}$ is independent (within the experimental error) of the concentration of the mannite up to 0.4 molal, and of the concentration of the hydrochloric acid up to 1.5 molal. The same conclusion holds for the results obtained with resorcin, but the value seems to be somewhat higher. This may be due, as the author suggests, to a combination of some of the resorcin with the ions, and the more or less progressive change with the concentration of the resorcin at the higher concentrations would seem to support this view. In view, however, of the uncertainty with respect to the temperature and of the fact that the results obtained with resorcin are probably not so accurate as those obtained with mannite, it seems best to adopt the value, $\frac{\Delta n_w}{\Delta n_s} = 0.28 \pm 0.04$, as the most probable one. The most probable values of the transference numbers are, similarly, $T_i^c = 0.844$, $T_i^a = 0.156$.[2]

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[1] See previous communication, this QUARTERLY, 21, 175 (1908).

[2] Buchböck treats his result in a somewhat different manner. Using the means, he extrapolates his hydration values to zero concentration, both of the hydrochloric acid and of the reference-substance. Although, as the table indicates, there seems to be a somewhat regular change in the mean hydration values, $\frac{\Delta n_w^c}{T_i^a}$, with the concentration, an extrapolation to infinite dilution seems not to be exactly warranted, in view of the variations in the values obtained at the two electrodes. It seems better to adopt a mean value from the data for the more dilute solutions and to conclude that, in moderate concentrations of HCl (up to, say, 1.5 molal) and with the concentration of the reference-substance so small that it does not appreciably change the activity of the water (say up to 0.3 molal), the results obtained both for transference number and for relative hydration are independent of the concentration of both electrolyte and reference-substance within the experimental errors.

The final values adopted for HCl are given by the following equations:

$$0.844\,N_w^{H^+} - 0.156\,N_w^{Cl^-} = 0.24 \pm 0.04,$$

$$\text{or} \quad N_w^{H^+} = (0.28 \pm 0.04) + 0.185\,N_w^{Cl^-}.$$

XII. Discussion of the Results

The *facts* which have been thus far established may be stated thus: *The electrolysis of a solution of potassium, sodium, or lithium chloride, or of hydrochloric acid, containing a nonelectrolyte at low concentration, is attended by an increase in the concentration of the nonelectrolyte at the anode and a corresponding decrease at the cathode, but no change in concentration takes place in the absence of the electrolyte.* These results are open to but two possible interpretations: (1) the reference-substance is carried by the electrolyte from cathode to anode, or (2) water is carried by the electrolyte from anode to cathode during the passage of the current.

The former hypothesis involves the assumption of the formation of a complex between the reference-substance and the chloride-ion in each case. This assumption alone is not sufficient, however, since it requires that the result obtained shall depend only upon the concentration of the chloride-ion, and shall be independent of the nature of the cation. The experiments with raffinose in solutions of potassium, sodium, and lithium chlorides show that this is not at all the case. In order that the first hypothesis shall explain the results, it is therefore necessary to assume, not only the formation of a complex with the chloride-ion in each case, but also the formation, but to a less degree, of a complex with the cation, the amount of the latter complex varying with the nature of the cation and increasing in the series Li, Na, K. This involves, moreover, in the case of sodium chloride, the assumption of the same kind and degree of complex formation with the ions in solutions containing substances of such highly different character as raffinose and arsenious acid. Similarly, in the case of hydrochloric acid, the two very different substances, mannite and resorcin, must unite practically in the same way with the ions of hydrochloric acid in order to explain the facts according to the first hypothesis. Moreover, Buchböck's experiments show that an increase of *300 per cent.* in the concentration of the nonelectrolyte or of *50 per cent.* in the concentration of the hydrochloric acid is without

appreciable influence upon the results, which obviously could not be the case if the ions were forming complexes with the nonelectrolyte.

In order to explain by this hypothesis the concentration changes resulting when a solution of potassium chloride containing sucrose is electrolyzed, it is necessary to assume that more sucrose is combined with chloride-ion than with potassium-ion. This state of things might result in two ways, as shown by the following equilibria:

$$\begin{aligned} C_{12}H_{22}O_{11} \quad &+ K^+ = [K(C_{12}H_{22}O_{11})]^+ \\ C_{12}H_{22}O_{11} \quad &+ Cl^- = [Cl(C_{12}H_{22}O_{11})]^- \end{aligned} \qquad (1)$$

$$\begin{aligned} x(C_{12}H_{22}O_{11}) &+ K^+ = [K(C_{12}H_{22}O_{11})_x]^+ \\ y(C_{12}H_{22}O_{11}) &+ Cl^- = [Cl(C_{12}H_{22}O_{11})_y]^- \end{aligned} \qquad (2)$$

In the first case we must assume that more of the chloride-ion-sucrose complex is formed than of the potassium-ion-sucrose complex. In the second case we must assume that y is greater than x, and sufficiently greater to give always more sugar in combination with the chloride-ion. In either case, application of the Mass-Action Law shows that increasing the concentration of the sugar will affect the two equilibria differently, the chloride-ion complex increasing at a more rapid rate than the potassium-ion complex. The mobilities of the two ions will, therefore, not change at the same rate, and the conductivity of a potassium chloride solution with varying concentrations of sucrose in the solution should be some other function than a linear one. The accompanying plot (Fig. 3), obtained by Masson and Martin,[1] shows no indication of any such combination of sucrose with the ions, the effect of the presence of the sucrose being simply to increase the viscosity of the medium and slow up both ions. In this figure, in which the curve for hydrochloric acid is also given, values of the equivalent conductivity, λ, are plotted as abscissæ and molal concentration of sucrose as ordinates.

The first hypothesis may therefore be considered as eliminated so far as any considerable effect is concerned.[2] The results obtained must, therefore, be due to the migration of water with the current; and, since the presence of the electrolyte is necessary to produce the result, we must assume some sort of a complex between the water and one or

[1] Masson and Martin, J. Chem. Soc., 79, 707 (1901).

[2] It is, of course, possible that the numerical values obtained are affected to some extent by a slight tendency on the part of the reference-substance to combine with the ions. Such an effect, if present at all, is probably very small, however. This is readily understood, since the active mass of the reference-substance is very small compared with that of the water (about 1 to 500).

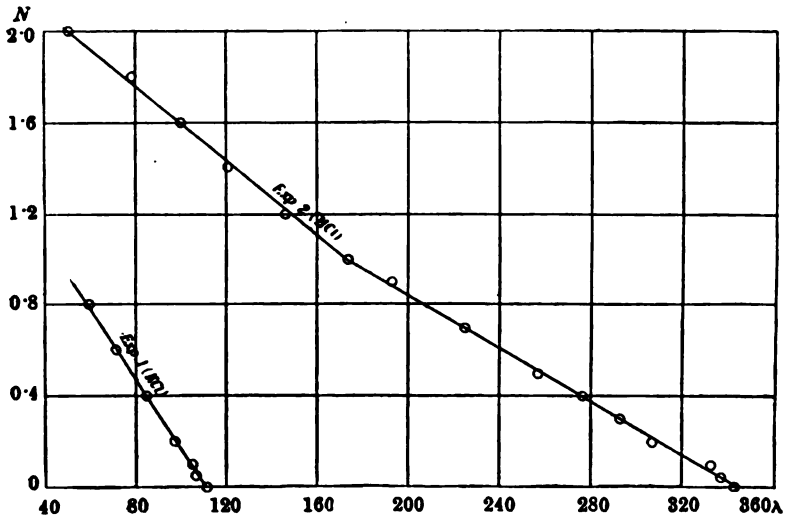

FIG. 3

both ions in each solution. This assumption is entirely in accord with all the results, and moreover serves to explain a number of facts in connection with the Ionic Theory which would otherwise be difficult to understand.[1]

Let us now consider the results as interpreted quantitatively upon the basis that the reference-substance does not migrate at all during the passage of the current. The results presented above for all the different electrolytes are collected in Table VI.

TABLE VI[1]

Electrolyte. Conc. 1 to 1.5 *M.*	$\frac{\Delta n_w^F}{T_t^c}$.	Δn_w^F.	T_t^c.	T_∞^c.	T_σ^c
HCl	0.28 ± 0.04	0.24 ± 0.04	0.844	0.83	0.82
KCl	1.3 ± 0.2	0.60 ± 0.08	0.495	0.495	0.482
NaCl	2.0 ± 0.2	0.76 ± 0.08	0.383	0.396	0.366
LiCl	4.7 ± 0.4	1.5 ± 0.1	0.304	0.330	0.278

[1] In this table, as well as in previous instances, the values given are the *means* of the two results obtained from each electrode independently. The deviation of this mean from the two individual values is indicated in each instance. Since most of the errors peculiar to transference experiments have a tendency to make the changes at the electrodes smaller in magnitude, if anything, than they should be, the deviations indicated may be considered as a fairly reliable measure of the maximum error of the results.

[1] For a full discussion of these facts in relation to the general problem of hydrates in solution, see Washburn, "Hydrates in Solution: A Critical Review of Recent Experimental and Theoretical Contributions to this Problem." Jahrb. Rad. u. Elec., December, 1908.

$$N_w^{H^+} = 0.28 \pm 0.04 + 0.185\, N_w^{Cl^-}. \quad (1)$$

$$N_w^{K^+} = 1.3 \pm 0.2 + 1.02\, N_w^{Cl^-}. \quad (2)$$

$$N_w^{Na^+} = 2 \pm 0.2 + 1.61\, N_w^{Cl^-}. \quad (3)$$

$$N_w^{Li^+} = 4.7 \pm 0.4 + 2.29\, N_w^{Cl^-}. \quad (4)$$

Absolute Hydration of the Ions

From the above equations, which give a relation between the hydration of the separate ions of each salt, the absolute hydration could be calculated if the value were known for any one ion. In Table VII the number of molecules of water combined with each ion is given for different assumptions regarding the number combined with the chloride-ion.

TABLE VII

MOLS OF WATER COMBINED WITH ONE MOL OF EACH ION

Cl^-.	H^+.	K^+.	Na^+.	Li^+.
0	0.28	1.3	2.0	4.7
1	0.46	2.3	3.6	7.0
2	0.65	3.3	5.2	9.3
3	0.83	4.3	6.8	11.6
4	1.02	5.4	8.4	13.9
5	1.2	6.4	10.0	16.2
6	1.4	7.4	11.6	18.5
7	1.6	8.4	13.2	20.8
8	1.8	9.5	14.9	23.1
9	2.0	10.5	16.6	25.3
10	2.1	11.5	18.0	27.6
11	2.3	12.5	19.4	30.2
12	2.5	13.5	21.3	32.2
20	5.0	21.7	34.2	50.5
. .	$\pm$ 0.04	$\pm$ 0.2	$\pm$ 0.2	$\pm$ 0.4

A glance at this table shows several interesting facts. The first row of figures evidently represents minimum values, since a negative hydration for the chloride-ion would have no meaning. The last row represents impossible values, since it requires that in a solution containing 1.2 mols of LiCl per 1,000 grams of water, approximately 70 mols of water must be combined with the two ions. Since such a solution contains only 55.5 mols of water altogether, the assumption of 20 mols of water on the chloride-ion is incorrect. Even the assumption of 12 mols of water combined with each mol of chloride-ion leads to the necessity of assuming that 44 out of a total of 55 mols of water is in combination with the ions, to say nothing of the amount in combination with the undissociated molecules. We may, at any rate, safely conclude that this row gives us maximum values.[1] It is therefore clear that all the cations in question are hydrated, that all those of the alkali elements are more hydrated than the chloride-ion, and that the hydration increases markedly between each successive member of the series, hydrogen, potassium, sodium, lithium.

Relations between the Hydration and the Conductance of Ions

The remarkable fact early attracted attention that in the case of elementary ions of any one group of the periodic system, those of smaller atomic weight possess a lower equivalent conductance, and therefore a smaller migration velocity. As a plausible explanation of this fact, it has been suggested[2] that the ions of the lighter elements are more hydrated (and therefore really larger and heavier) than those of the

[1] In order to decide which set of values to adopt, it is necessary to know some other relation between the hydration of the ions for some one of the above substances. As explained by the author in another place (*loc. cit.*, Jahrb. Rad. u. Elec.), if accurate data were available on the lowering of the vapor pressure at 25°, of say 0.5 molal solution of the above chlorides, a fair idea of the *total* amount of water in combination might possibly be obtained; and once this is known for any one salt, approximate values for the absolute hydration of all the above ions could be calculated. Vapor pressure data on several of the above chlorides would also make it possible to test the assumptions, since if these are correct the same values for the hydration of the ions should be obtained from the lowering of vapor pressure for each salt. It is to be hoped that such data will soon be available. It is, of course, possible to calculate the vapor pressure lowering at 25° from the data on the lowering of the freezing point if the heats of dilution are known. Data on the lowering of the freezing point and heat of dilution are available but are of doubtful accuracy, and it has not, therefore, seemed advisable to attempt the calculation of the total amount of combined water until accurate data are available. From the data at present available, we should conclude that the true values lie somewhere in the first six rows of Table VII.

[2] Bredig, Z. physik. Chem., 13, 277, No. 2 (1894); Euler, Wied. Ann., 63, 273 (1897); Kohlrausch, Proc. Roy. Soc., 71, 338 (1901).

heavier elements. This explanation has now for the first time, by the results of this research, received conclusive confirmation.

Table VIII contains comparative data for the three alkali elements investigated. The second column contains the atomic weight of the element; the third, its atomic volume in the solid state; the fourth, the equivalent conductance of its ion at 18° as derived by Kohlrausch; the fifth, a formula representing the minimum hydration consistent with the transference results (see first row of Table VII); the sixth, the corresponding molecular weight of this hydrated ion; and the last two columns, the apparent molecular volume of the chloride in solution, calculated from density data[1] by the hypothetical principle that the uncombined water in the solution has the same volume as an equal quantity of pure water at the same temperature, and under the special assumptions, first (under I), that none of the water is combined, and second (under II), that the quantity combined is that which corresponds to the minimum formulæ in the sixth column (chloride-ion being thereby assumed anhydrous).

TABLE VIII

Element.	At. wt.	At. vol.	Equiv. cond.	Formula of hydrated ion.	Mol. wt. of hydrated ion.	Apparent Mol. Vol. of Chloride in Solution.	
						I.	II.
Potassium	39.1	45.5	64.6	$K(H_2O)_{1.8}$	62.5	26.4	49.8
Sodium	23.0	23.7	43.5	$Na(H_2O)_{2.0}$	59.0	16.8	52.8
Lithium	7.0	13.1	33.4	$Li(H_2O)_{4.7}$	92.0	16.0	100.5

If a larger hydration be assumed (for example, that corresponding to 2 mols of water on the chloride-ion), the differences in the molecular weights of the ions and the molecular volumes in solution of the chlorides become still more pronounced.[2]

[1] See Ruppin, Z. physik. Chem., 14, 482 (1894); also Forch, Ann. Phys., 12, 591 (1903).

[2] In the above calculations of the apparent molecular volumes in solution, the assumption is made that the uncombined water in the solution has the same volume as in the pure state. This is probably not the case, as changes in the complexity of the water are also accompanied by changes in volume. Such changes would, however, probably be of the same order of magnitude in each of the above cases, so that the apparent molecular volumes in solution, thus calculated, for salts of one group, may still properly be used for purposes of comparison with one another. The values are for 0.25 molal solutions at 25°.

The present investigation has shown further that the values which have heretofore been obtained for the transference numbers of many, if not all, electrolytes in concentrated solutions by the Hittorf method are to be regarded as erroneous, since their calculation involves the assumption that the solvent remains stationary during the electrolysis. A glance at Table VI shows the error produced in the transference number by neglecting hydration. In the case of potassium chloride, instead of decreasing from 0.495 at infinite dilution to 0.482 at 1.2 molal, as heretofore assumed, the transference number is found to remain unchanged over this range of concentration. This is in entire agreement with the fact that the mobilities of the potassium and chloride-ions are very nearly the same, and consequently a change in the viscosity of the medium should affect the velocities of both ions about equally.

In the case of the other ions the change of the transference number with the concentration is much less than has heretofore been assumed. Thus in the case of sodium chloride it is from 0.396 to 0.383 instead of to 0.366; in the case of lithium chloride from 0.330 to 0.304 instead of to 0.278.

XIII. The Relation between the True and the Ordinary Transference Numbers

We have seen that the ordinary transference number (T_o) for concentrated solutions, as obtained by the Hittorf method, is erroneous in cases where the ions are hydrated, since it is calculated on the assumption that the water remains stationary during the passage of the current. A relation, however, exists between the quantity so calculated (T_o), the true transference number (T_t), and the number of mols of water (Δn_w^F) transferred per equivalent of electricity. The derivation of this relation will be readily understood from the following considerations. Let one equivalent of electricity be passed, for example, through a potassium chloride solution with a silver anode and silver chloride cathode. As a result, T_t^c equivalents of KCl and Δn_w^F equivalents of water are transferred from anode to cathode. As a result of the water transference, the ratio of salt to water at the cathode is not so great as it would be if no water were transferred. Consequently, if the whole concentration change be attributed to the transfer of salt alone, the number of mols of salt transferred by the current will appear smaller than it really is. It should be increased by the amount of salt originally associated with

the water transferred. This amount is obviously the quantity, $\Delta n_w^F \frac{n_s}{n_w}$, where $\frac{n_s}{n_w}$ is the ratio of mols of salt to mols of water in the original solution. When this correction is made we obtain the relation,

$$T_t^c - T_o^c = \Delta n_w^F \frac{n_s}{n_w}.$$

This is an important equation; for, since the ordinary transference number (T_o) is usually known or can be determined experimentally by the Hittorf method, this equation offers a means of calculating either the true transference number (T_t), or the water transference (Δn_w^F), provided the other is known. By the method of the present investigation all three quantities are directly measured. Other methods are available, however, which give the value of either T_t or Δn_w^F alone.

Lewis[1] has recently described a method for obtaining the quantity, Δn_w^F. The principle of this method consists in measuring the potential of a concentration cell, both solutions of which are saturated with the electrolyte, the latter being only sufficiently soluble to form a dilute solution. One of the solutions, however, contains in addition a certain amount of some nonelectrolyte, so that the vapor pressure of the water is different on the two sides of the cell. If the nonelectrolyte does not combine with the ions, the only change attending the operation of such a cell would be the transfer of water from one solution to the other. The potential of the cell would therefore be a direct measure of the work done in transferring the water; and the amount so transferred (Δn_w^F) could be calculated from the relation of this work to the known work involved in transferring one mol of water from a solution with one vapor pressure to a solution with another vapor pressure. This method is now being applied experimentally in this laboratory.

It has been shown by Mr. R. C. Tolman, who is now investigating it in this laboratory, that the centrifugal method of des Coudres[2] gives directly the true transference number. In this method a solution of the electrolyte is placed in the tube of a centrifugal apparatus and rotated at a high speed. As a result of the unequal mobilities and densities of the two ions, an electromotive force is set up between the

[1] Lewis, Z. Electrochem., 14 (1908); J. Am. Chem. Soc., 30, 1355 (1908).

[2] Wied. Ann., 49, 284 (1883). See also his gravitation method involving the same principles, *ibid.*, 57, 232 (1896).

inner and outer ends of the tube and can be measured by the use of suitable electrodes. From the principles of thermodynamics an equation can be derived connecting this electromotive force with the speed of rotation, the distances of the inner and outer electrodes from the centre of rotation, the partial volume of the electrolyte and of the electrode material in the solution, and the true transference number. Since all the other quantities are capable of measurement, the true transference number can be calculated. No sufficiently accurate data are yet available, however.

Another method for obtaining the true transference number is the method of moving boundaries. This method has recently been so perfected by Denison and Steele[1] as to equal in accuracy the Hittorf method. In dilute solution the true transference number and the ordinary one as obtained by the Hittorf method are identical, as is evident by referring to the equation connecting them (since the ratio $\frac{n_s}{n_w}$ is then very small). Denison and Steele found, in fact, that all their results for dilute solutions agreed satisfactorily with those obtained by the Hittorf method. In concentrated solutions, however, large deviations were observed, which these investigators were unable to explain. Thus, they remark: "Wir haben die Messungen öfters widerholt, aber immer mit demselben Resultat, und zwar 0.508 bis 0.510 für die Anionüberführungszahl von 1.0-norm. KCl und 0.613 bis 0.615 für 1.0-norm. NaCl. Die allgemein angenommenen Werte dieser Grössen sind etwa 0.514 für 1.0-norm. KCl und 0.63 für 1.0-norm. NaCl. Der Grund dieser Abweichung muss vorläufig dahingestellt bleiben; für unsern Zweck genügt es aber, dass schon in 0.1-norm. Lösungen der Unterschied zwischen unsern Zahlen und den durch die analytische Methode gelieferten nicht mehr besteht."

The explanation for this difference between the values obtained by Denison and Steele and the Hittorf values is now apparent: *The rate of motion of the ion-boundary through the solution is a direct measure of the true transference number*[2]; consequently, the results obtained

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[1] Denison and Steele, Z. physik. Chem., 57, 110 (1906).

[2] It is true that when the motion of the boundary is measured, as in the experiments of Denison and Steele, by means of a reference point outside of the solution, any displacement of the solution as a whole through volume changes accompanying the electrode processes would affect the apparent rate of motion of the boundary. The authors state, however, that in the case of their experiments, there was not an appreciable change of volume as a result of the electrode process.

by this method should differ from those obtained by the Hittorf method for concentrated solutions. It is therefore interesting to compare the results obtained by Denison and Steele with the values obtained in the present investigation. These are brought together in the following table (Table IX). The values are those for the cation.

TABLE IX

	True Transference Number.		Ordinary Transference Number.
Salt.	Denison and Steele.	Washburn.	Washburn.
KCl	0.492[1]	0.495[2]	0.482
NaCl	0.386[1]	0.383[2]	0.366

[1] For a molal solution at 18°. [2] For a 1.25 molal solution at 25°.

When the difference in temperature and concentration is considered the agreement seems to be satisfactory.[1] Denison and Steele also obtained the same transference number for molal and for 0.1 molal potassium chloride solutions, which agrees perfectly with the result of the present investigation.

By measuring true transference numbers by the method of moving boundaries and "ordinary" transference numbers by the Hittorf method, it is obvious that we are in possession of an excellent method for determining the relative degrees of hydration of the ions, a method which does not require the presence of any third constituent in the solution and which is free from all arbitrary assumptions. Future investigations in this direction seem to offer the most promising line of attack upon the problem of hydration in solutions of electrolytes.

XIV. Summary

1. This investigation has shown that the electrolysis of a solution of potassium, sodium, or lithium chloride, containing a nonelectrolyte at low concentration, is attended by an increase in the ratio of the quantity of nonelectrolyte to that of the water at the anode and by a correspond-

[1] Denison and Steele found that the values they obtained for concentrated solutions varied somewhat with the nature of the "indicator salt," so that the method must be pursued further, experimentally, before a final decision can be arrived at regarding the correct values for concentrated solutions.

ing decrease at the cathode, but that no change takes place in this ratio in the absence of the salt.

2. It is shown that this change is to be attributed mainly, if not wholly, to a transfer of water from the anode to the cathode during the electrolysis.

3. By referring the changes in the content of water and of salt to the nonelectrolyte as a reference-substance, a relation between the degrees of hydration of the chloride-ion, the lithium-ion, sodium-ion, and potassium-ion has been derived. A similar relation involving the hydrogen-ion had been previously obtained by Buchböck.

4. The results show that all these cations are hydrated; that the hydration increases markedly between each two members of the series H^+, K^+, Na^+, Li^+; and that the smallest values of the hydration consistent with the data are represented by the formulæ: $[H(H_2O)_{0.3}]^+$, $[K(H_2O)_{1.3}]^+$, $[Na(H_2O)_{2.0}]^+$, and $[Li(H_2O)_{4.7}]^+$. The hydration of all these ions may, however, be considerably greater than these values.

The fact that the ions of the elements of a group of the periodic system increase in migration velocity with increasing atomic weight has heretofore been explained by assuming that the ions of the lighter elements are more highly hydrated. The correctness of this explanation has been demonstrated by the results of this research.

5. It is further shown that, owing to the transfer of water during the electrolysis, the transference numbers hitherto obtained for the more concentrated solutions of these chlorides are erroneous, since the calculation involved the assumption that the water remained stationary. The true transference numbers, derived by reference to the nonelectrolyte, are found to vary with the concentration much less than the apparent ones previously computed. In the case of potassium chloride, there is no variation whatever up to a concentration of 1.2 molal.

6. A mathematical relation between the true transference number and the ordinary one as obtained by the Hittorf method is derived. It is also pointed out that the method of moving boundaries gives the true transference number. The results of Denison and Steele obtained by this method are compared with the true transference numbers obtained in the present investigation and shown to agree. Attention is called to the fact that the combination of transference numbers obtained by the Hittorf method with those obtained by the method of moving boundaries furnishes a very promising method for further investigating the hydration of ions.

In conclusion, I desire to express my great indebtedness to Professor A. A. Noyes, whose interest, coöperation, and encouragement throughout the progress of this investigation have made possible its successful completion.

To the Carnegie Institution of Washington, whose financial assistance has made possible the continued prosecution of the research, grateful acknowledgments are also due.

BOSTON, MASS., July 1, 1908.

CONTRIBUTIONS FROM THE
LABORATORY OF SANITARY CHEMISTRY

METHODS OF TESTING THE EFFICIENCY OF VENTILATION

BY ELLEN H. RICHARDS, E. MARION WADE, ROYCE W. GILBERT,
CARL E. HANSON, JAMES M. TALBOT

THE application of scientific knowledge to the daily living conditions of human beings is demanded today as never before. We are slowly learning that these applications may be made without, in all cases, using the time-consuming methods of exact science. It is a working basis for the betterment of conditions that is demanded, and a more general use of the facts as fast as learned.

Especially is this true of the examination of the air supply of rooms, shops, dining halls, and places of amusement and of study.

The general quality of the air is in question. Is it fit for human beings to breathe? The facts brought out in the course of the crusade against tuberculosis show that in a far too large number of circumstances the general conditions are dangerous, and that a concerted effort must be made to interest the people to better them.

To secure these general facts in a sufficient number of cases requires methods which shall be reliable and accurate within limits, and not so time-consuming as to be prohibitive.

A systematic effort has been made to meet this want by the classes studying Air Analysis at the Institute of Technology; namely, Course II, Mechanical Engineering, Option 4; Course V, Chemistry; Course VII, Biology; and Course IX, Sanitary Engineering. Some results of the past two years' experience are here given.

A general consensus of opinion among recent investigators points to recorded temperature as the most practicable means of controlling ventilation under modern conditions. The temperature of any given room may increase by any one or any combination of the following causes: (1) Heat given off by the bodies of the occupants and by their breath;

(2) Heat given off by the lights: (3) Rise of outside temperature; and (4) An excess of heat from the heating plant.

The last of these causes should be practically eliminated in a modern, well-constructed, and well-managed public structure. Of course the average private home has not yet reached this point of refinement in the perfection of its heating system, but it is not the small individual house or even the apartment house that is usually in need of ventilation. In a small room with few occupants, the doors, windows, and cracks usually provide sufficient change of air. It is in the large halls, office buildings, schools, etc., where many persons are congregated under one roof, that ventilation is most needed and inspection of ventilation is most important. In all such places the heating system is, or should be, designed to deliver a constant amount of heat for any given period of time.

Contrary to the old theory that a heating plant should "keep a room at a given temperature," and so automatically supply less and less heat as the heat derived from the occupants increases, the new idea is rather that the plant deliver a constant predetermined amount and that the ventilating plant keep the room at the desired temperature. This idea is really carried out in most of the buildings with which the ventilating engineer or inspector would have to deal. This being the case, any rise of temperature in a room would be caused by the animal heat of the occupants, effect of the lights, or by rise of the outside temperature. This last cause is slight in any instance and may usually be neglected.

Then, since in giving off heat the body and the lights (with the exception of electric incandescent) give off both CO_2 and moisture in proportion, we have in this increase in temperature an almost ideal index of the quality of the air. A recording thermometer with a large dial face, hung or placed so as to be as readily seen as a clock, is the best known gauge of an occupied room.

If the air current through an occupied space is sufficient to carry away the increased moisture and to keep the temperature even, it will lower the carbon dioxide in the same proportion. This may be accepted as true without chemical examination (there are occasionally other sources of CO_2). The humidity is therefore an excellent indicator of the degree of ventilation, and a recording hygrometer is most desirable to place alongside the recording thermometer. Frequent observation and record may replace these rather expensive instruments to a degree.

We feel safe in stating that probably the best engineering practice

in ventilation today is in the use of these instruments, combined with training in the detection of odors. Only in cases of control or inspection will the determination of CO_2 be necessary when these instruments are at hand and when time for observing them is available. But there are frequent circumstances in which CO_2 is an equally good indicator and the tests for it more convenient of application, but they should partake of the rapidity and comparative accuracy of the instruments, and should not require the engineer to be burdened with cumbersome apparatus. For these purposes a sufficient degree of accuracy may be defined as within two-tenths to three-tenths of a part per 10,000, with a possible maximum error of five-tenths.

It does not seem to be possible in the present state of our knowledge to devise chemical tests for carbon dioxide which may be put with safety into the hands of unskilled persons, as may thermometers, but chemists and trained inspectors may use one of the following methods with confidence in their accuracy after a considerable practice, always using *outside air as a standardizing* medium. This will show at once any errors due to changing strength of the testing solution or fault in the manipulation.

The testing solution is not only carefully prepared, but protected against change while using by clamping the rubber stopper with a screw, or, in the case of additional bottles to be transported, by covering the stoppers with paraffin. The mounted automatic pipette ("Air, Water, and Food," page 42) is most convenient, but the inspector may mount an ordinary burette to answer the same purpose of delivering a measured 10 c.c. of solution.

The apparatus most used for this purpose in recent years is the Fitz or the Wolpert "shaker" ("Air, Water, and Food," page 43), a graduated glass tube in which successive small quantities of air are brought into contact for a definite time (thirty seconds) with a known volume of standard lime water, using the same solution for each partial sample of air, until the color of the indicator disappears. The relation between the quantity of CO_2 present and the total amount of air required to decolorize 6.3 c.c. of a standard saturated solution is shown in Table A.

TABLE A — FITZ SHAKER, PISTON, OR CYLINDER. 6.3 C.C. SATURATED LIME WATER PER LITER

Cubic centimeters of air.	Parts CO_2 in 10,000.
50	15.6
70	12.4
90	10.2
110	8.7
130	7.5
150	6.6
170	5.8
190	5.2
210	4.8
230	4.5
250	4.3
270	4.1
290	3.95
310	3.8
330	3.7
350	3.6

The taking of successive portions at even this short interval involves errors in sampling which in unskilled hands are liable to be serious. There is also an irregularity of action due to the fact that, as the solubility of a gas from a gaseous mixture is proportional to its partial pressure, the first portion of air gives up a larger part of its CO_2 than the later portions, in the same time; and therefore a much longer time should be allowed for absorption, which is not very practicable.

This property of gases is utilized, however, in another manner by the method of Cohen and Appleyard, in which the lapse of time is used to indicate the amount of CO_2 present in the mixture. This method, based as it is on a well-known scientific principle, has not received the attention it deserves; although it has been experimented with until it is, we think, on a workable basis.

The following methods of collecting the sample may be used according

to circumstances and may be described as (*a*) the water siphon; (*b*) the piston apparatus; (*c*) the steam-caused vacuum.

The alkaline solution is the same whatever method of collection is used and is made from a saturated solution of "lime water" of whatever strength is desired. 2.5, 5, and 10 c.c. to the liter are most available, according to the character of the air to be tested, the medium strength being of most general usefulness. Sodium or potassium carbonate, which readily takes on another molecule of carbon dioxide, may be substituted, whenever weighing out the pure solid is preferable to preparing the lime water. There may be also a slight increase in rapidity of action. These acid carbonate solutions keep better than caustic standards.

(*a*) *The Water Siphon Method.*—Two bottles (diameter one-third the height) of nearly equal capacity are fitted with rubber stoppers carrying small glass tubing, connected by several feet of rubber connector, with clamps (Fig. 1). One bottle is completely filled with water, nearly free from carbon dioxide.

The pair of bottles is taken to the place from which the air is to be collected. The inlet tube may be long to reach to near the ceiling, or short; if long, the first siphoning should be rejected, to secure filling the inlet tube with the air desired, the stoppers exchanged, and the sample taken. The air-filled bottle is stoppered and taken to the laboratory; or the test solution is at once added, the bottle stoppered and shaken, noting minutes and seconds. One bottle of water with a small reserve will serve for a number of takings before absorbing a deleterious amount of CO_2.

(*b*) *The Piston Method.*—In the piston method a glass cylinder containing approximately 600 c.c. is used. The two ends of the cylinder (Fig. 2) are of brass, one being pierced by a stopcock to admit the air to the tube, and the other by the connecting rod of the piston, which is made to fit the walls of the cylinder as closely as possible. The piston must be tight against the bottom of the cylinder. Then, with the apparatus at arm's length, the stopcock in the bottom is opened, and with a steady pull on the connecting rod the cylinder is filled with the desired air, care being taken to pull the piston tight against the upper end of the cylinder. After closing the stopcock the cylinder is ready to be taken to the laboratory for testing.

10 c.c. of lime water solution, colored by phenolphthalein, is run into the cylinder and the stopcock immediately closed. The tip of the burette, containing the 10 c.c. of lime water, is held at the lip of the stopcock

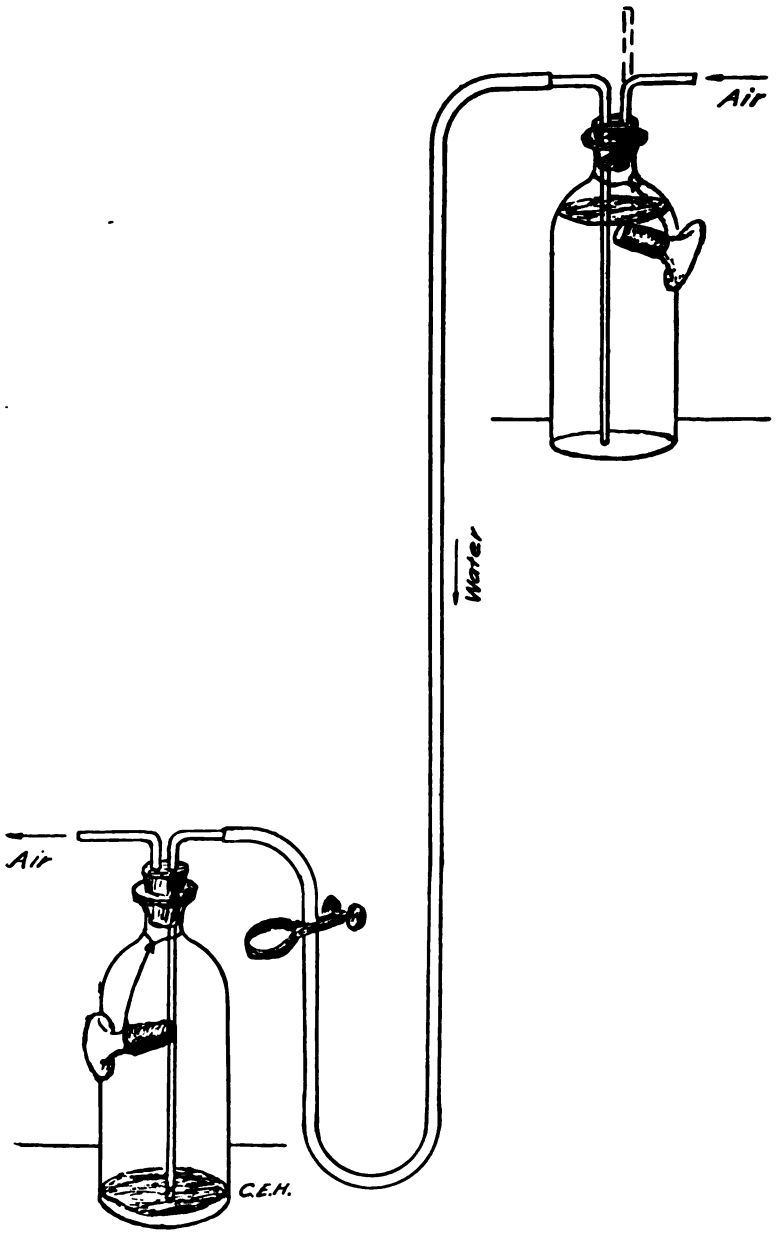

FIG. 1.— WATER-SIPHON APPARATUS

(made with a lip for the purpose), and the solution runs down the interior sides of the stopcock as the displaced air comes out of the centre. The number of seconds of gentle shaking before the color of the indicator disappears over white paper is recorded. This method may be used for samples taken by the siphon or vacuum methods, as well as the piston. From the known strength of the solution and the time, the number of parts of CO_2 per 10,000 may be read from the table.

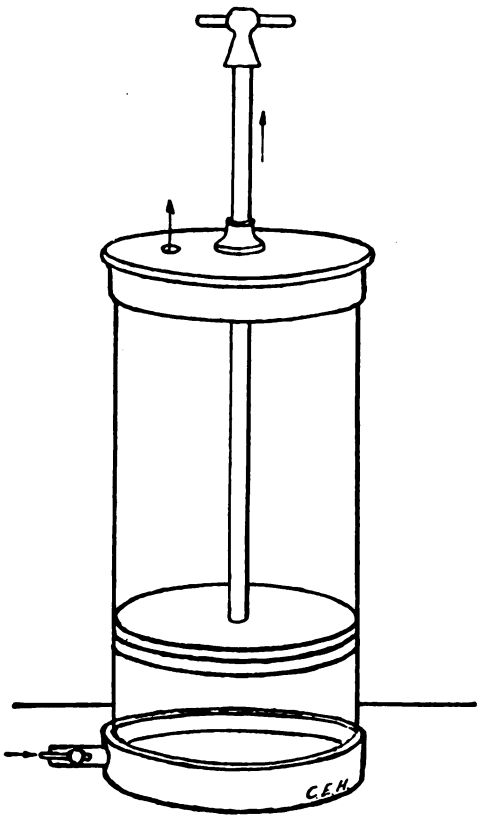

FIG. 2.—CYLINDER WITH PISTON

TABLE B — TIME METHOD. SAME SOLUTION AS IN TABLE A

TIME.		Parts CO_2 in 10,000.
Minutes.	Seconds.	
0	30	15.6
0	45	12.1
1	0	9.9
1	15	8.4
1	30	7.2
1	45	6.3
2	0	5.5
2	15	4.9
2	30	4.4
2	45	4.0
3	0	3.8
3	15	3.7
3	30	3.6

(*c*) *The Steam Vacuum Method.*—The steam is supplied by a 500 c.c. flask serving as a boiler, with a Tirrill burner to supply the heat. The flask (Fig. 3) is fitted with a rubber stopper carrying a No. 6 glass tube, bent so that one end extends within ½ inch of the bottom of the bottle when placed in position on the stand. The bottles used are of about 500 c.c. capacity, made for a ground-glass stopper but fitted with a rubber stopper.

To prepare the jet, the water in the flask is allowed to boil for five minutes in order to expel completely the air in the water and the flask. The pressure should be sufficient to throw the vaporized steam at least 1 foot above the exposed end of the tube.

The empty bottle is placed on the stand in an inverted position and allowed to remain for three minutes. In the meantime a thin coating of vaseline is applied half way up the sides of the stopper. The vaseline acts as an unguent, reducing the coefficient of friction to such an extent that the principal resistance is due to the reaction of the stopper against

compression. This enables one to force the stopper in far enough to bring the glass and rubber into intimate contact, which is essential. The vaseline also fills the interstices between the rubber and the glass, which makes leakage impossible.

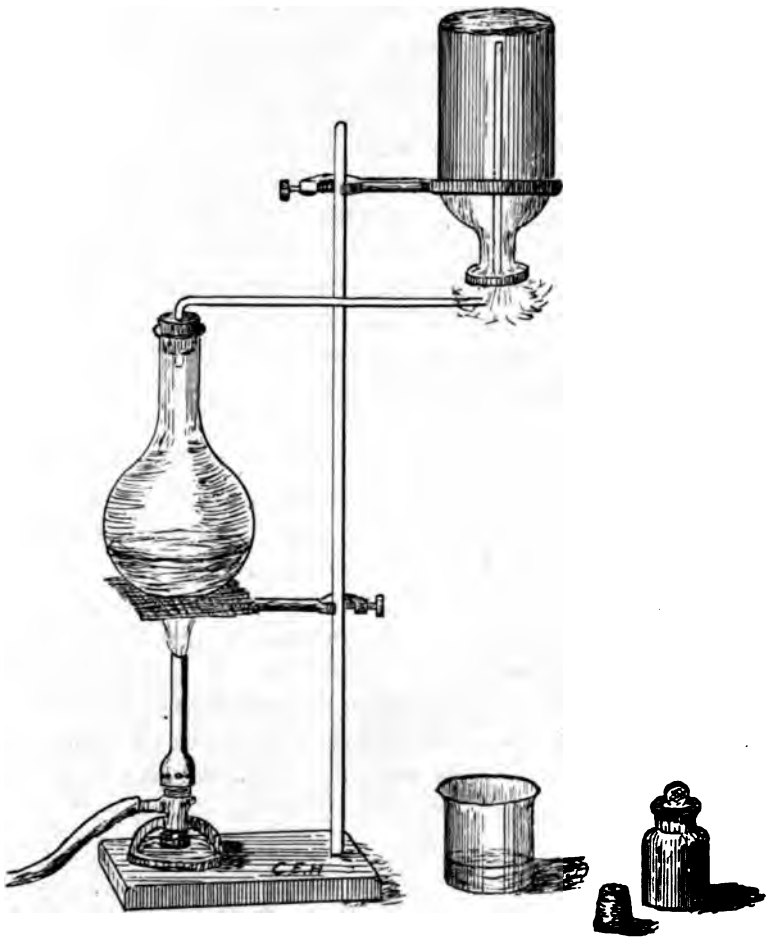

FIG. 3.— STEAM-VACUUM APPARATUS
From the thesis of Carl E. Hanson, 1908

Protecting the hand with a cloth, the bottle is raised from the stand, and the instant it clears the end of the tube the stopper is inserted while the bottle is still inverted. The stopper may be pushed in more securely by pushing it against the table with a few pounds' pressure while the bottle is still in the inverted position. The stopper is kept in under this pressure for a few minutes until the vacuum begins to form, after which the atmospheric pressure will keep it in place.

All the bottles required are treated in the same way. The rubber stoppers should be at least one size larger than would ordinarily be used for the bottles, and should project three-eighths of an inch or more to be easily removed when the sample is to be taken.

Sample bottles may be tested for completeness of vacuum by holding them in an inverted position under water at 70° F., free from carbon dioxide, and removing the stopper. After the water has replaced the vacuum, the stopper is inserted and the bottle removed.

Testing the Apparatus.—For the testing of the methods we have used the "live box," or air-tight room, devised in 1897 by Herbert E. Smith for his thesis on schoolhouse ventilation. Small weighed candles are placed in a flat-bottomed glass dish, lighted, the box closed and screwed tight, and the candles allowed to burn out. The electric fan is kept running to mix the air. After an hour samples may be drawn from the space at any of the three different levels desired, through glass tubes which the box carries. The following are examples of tests made in this manner.

Two candles three-eighths of an inch long and weighing six-tenths of a gram each were burned in a box containing 12 cubic feet of air. The candles burned for five minutes, and the resulting carbon dioxide content was from twenty to twenty-eight parts.

Two candles 2 inches long and together weighing 6.8 grams, burned in the large box (cubic contents 86.625 cubic feet) for forty-five minutes, produced an air containing thirty parts CO_2.

That the air in the box is uniformly charged with CO_2 (when the fan is running) and that it remains constant is shown by the following times of neutralization by the time method. These samples were taken at different times during the same day:

Trial.	Whole Solution.	Half Solution.
	Time.	Time.
	Seconds	Seconds
1	15	25
2	15	25
3	15	23
4	15	23
5	15	25

The outdoor air has too low a carbon dioxide content to serve for the test of an apparatus designed to detect larger quantities, and the air of well-ventilated rooms, as most of the schoolrooms are, is not only too good, but subject to too many variations to serve as reservoirs of constant air. The "box" has served us well in these respects, and with weighed candles repetition of the tests is easy. The air may remain constant for two weeks if only the small quantities are removed.

Interpretation of Results.—If in a crowded hall the temperature is less than 70° F., if the wet and dry bulb thermometers are 7° apart (less than 70 per cent. humidity), with no appreciable odor, and if the carbon dioxide is less than seven parts per 10,000, the air may be said to be satisfactory; but if the temperature is 80°, the wet and dry bulb only 4° apart (humidity 83 per cent.), and the carbon dioxide eight parts, with a close odor, then measures should be taken at once to remedy the condition.

The ideal condition for constant occupancy is: thermometer 68°, humidity 68 per cent., or wet and dry bulb 6° to 7° apart, with carbon dioxide less than six parts per 10,000 of air.

If these general results may be obtained, the smaller differences in readings may be discarded until the public is educated to this extent.

BOOK REVIEWS

Rocks and Rock Minerals[1]

Few if any petrologists are better qualified by reason of notable attainments in the science, as well as by long experience in teaching it, to write a manual of petrology than is Professor Pirsson, of Yale University, and it is with pleasure that we note the appearance of the book before us. Teachers of petrology will in general, we believe, fully agree with the author's opinion as expressed in his preface, that there has long been a need for a "small, concise, and practical treatise" on petrology in which the subject is dealt with entirely from a megascopic standpoint. Mining engineers and others who have to deal with rocks in a practical way have also felt the urgent need of such a book for purposes of reference. In our opinion the present manual meets this need in a highly satisfactory manner, and its publication marks a distinct advance in the treatment of elementary petrology. A general idea of the scope of the book may be obtained from the table of contents which follows:

Part I. *Introductory and General Considerations.*

Chapter I. Scope of Petrology: Historical Methods of Study.

Chapter II. Chemical Character of the Earth's Crust and Its Component Minerals.

Part II. *Rock Minerals.*

Chapter III. Important Properties of Minerals.

Chapter IV. Description of the Rock-making Minerals.

Chapter V. Determination of the Rock-making Minerals.

Part III. *The Rocks.*

Chapter VI. General Petrology of Igneous Rocks.

Chapter VII. Description of Igneous Rocks.

Chapter VIII. Origin and Classification of Stratified Rocks.

Chapter IX. Description of Stratified Rocks.

[1] Rocks and Rock Minerals. A Manual of the Elements of Petrology without the Use of the Microscope. By Louis V. Pirsson. New York: Wiley. London: Chapman. 414 pp., 74 il., 36 pls., 12mo.

Chapter X. Origin, General Characters, and Classification of the Metamorphic Rocks.

Chapter XI. Description of the Metamorphic Rocks.

Chapter XII. The Determination of Rocks.

Index.

The arrangement of the material in the various chapters is admirable throughout, while discussions, descriptions, and statements in general are accurate, clear, concise, yet sufficiently complete, and are written in a style which is attractive and easy to read. Chapter IV, dealing with the general petrology of the igneous rocks, seems particularly worthy of notice, since it presents such material of a general character, both practical and theoretical, as is really essential for a clear understanding of igneous rocks in a manner entirely in keeping with the most recent developments of the science, and yet within the comprehension of those not thoroughly trained in physical-chemistry, nor in microspetrology—a task that is not an easy one. An idea of the contents of this chapter will be gathered from the following topics, which are among those discussed therein: The modes of occurrence of igneous rocks; the chemical composition of magmas and their differentiation; the crystallization of silicate solutions (magmas) and the development of texture in igneous rocks; contact metamorphism; the classification of the igneous rocks.

In regard to the classification mentioned above, a system has been developed entirely consistent with megascopic petrology, all distinctions being based upon differences of texture or of mineral composition that can be made out by the careful study of good hand specimens with the aid of a pocket lens and a knife, in some few instances supplemented by a simple chemical test. The first division is made on the basis of differences of grain (granularity) into three classes. These are further divided according as the rock in question is porphyritic or non-porphyritic. Further division is made, chiefly upon differences of mineral composition, into a few broad groups which are designated by familiar rock names (granite, diorite, etc.) firmly fixed in petrological literature by long usage. The more important varieties falling under these various groups or kinds of rock, but which for microscopical or other reasons have received special names from petrographers, are referred to in appropriate places, so that the significance of such names when encountered can be easily found by reference to the book. Among the names adopted for the rock groups it may be noted that dolerite has been retained, very wisely it seems, to designate those granular, igneous rocks with predomi-

nant ferro-magnesian minerals, but in which it is not possible to tell positively just what ferro-magnesian mineral is present. This group will therefore include much that is commonly referred to as diabase. Felsite (or felsite-porphyry) is used for those nearly or entirely dense rocks, light in color, and generally highly feldspathic in character, while basalt (or basalt-porphyry) covers those dense, dark-colored, igneous rocks, for the most part ferro-magnesian in character. It will be noted that both of these terms, felsite and basalt, have been given a broader meaning than is customary in books covering a somewhat similar field. For example, dacites and most andesites fall under the head of felsite. Directions, however, for recognizing such varieties, when it is possible to do so microscopically, are given. The classification is summarized in a convenient table.

While some teachers will doubtless wish to make minor additions to the scheme of classification in their classroom work, the scheme as a whole appears so sane, simple, and practical that it can hardly fail to meet with general approval, and it is to be hoped that it will also come shortly into general use. In such an event it would be a strong influence toward uniformity and simplicity of practice among field workers in geology and petrology.

In Chapter VII we find the descriptions of individual kinds of rock treated under such appropriate headings as: Mineral Composition; General Properties; Chemical Composition (the latter illustrated by a few well-chosen analyses); Occurrence and Alteration. Thus while the descriptions furnish one with data useful for the recognition of the rock in the field or laboratory, they also furnish in a most satisfactory manner what might be termed the Natural History of the rock.

With so excellent a manual available as a basis for petrological study, it is to be hoped that it may be substituted for the dry and generally uninteresting lecturing so common in petrological laboratories, as well as for the too numerous laboratory guides and notes of inferior quality, and thus promote a general improvement in petrological teaching.

In conclusion it may be said that the book is conspicuous by reason of its typographical excellence and for the superior quality of the illustrations, which illustrate the text admirably.

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Climate and Weather of Maryland[1]

Volume II of the Reports of the Maryland Weather Service appeared in June, 1908. This volume is devoted to a "Report on the Climate and Weather of Baltimore and Vicinity," by Dr. Oliver L. Fassig.

The report is divided into two portions, the first dealing with the climate of Baltimore, including atmospheric pressure, temperature of the atmosphere, humidity, precipitation, sunshine and cloudiness, the winds, and electrical phenomena.

The second portion, the weather of Baltimore, deals largely with storms. There is a general discussion of cyclones and anti-cyclones, weather charts of the Northern Hemisphere, and the principal climatic zones. This is followed by chapters on winter weather, including various types of storms and certain particular ones. The spring weather, the summer weather, and the autumn weather are discussed and illustrated in a similar way.

The final chapter of the book is an historical one on foretelling the weather.

This treatise is remarkably complete in all its details, and might serve as a text-book of meteorology. The value of the text is greatly enhanced by the numerous charts and graphic diagrams, besides many tables, giving data from 1876 to 1903.

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[1] Maryland Weather Service. Vol. II. Baltimore: Johns Hopkins Press, 1907. 515 pp., il., pls.

TECHNOLOGY QUARTERLY

AND

PROCEEDINGS OF THE SOCIETY OF ARTS

Vol. XXI DECEMBER, 1908 No. 4

EQUITABLE RATE-MAKING BY PUBLIC SERVICE COMPANIES

By DUGALD C. JACKSON

Read April 23, 1908

I. Principles Must Be Formulated

The problems of appropriately fixing rates to be charged by so-called public service companies for the service which they render have been given much quiet study in this country for a number of years. The officials of many companies have given them extended study. The Interstate Commerce Commission has been at it, and some state commissions have also been at it. But there has as yet been little advance made in the methods of treating the difficult problems.

The present storm of discussion, precipitated by the results following the policies of a few impetuous promoters who have secured control of some properties and the work of irresponsible or incapable managers in temporary charge of properties held legitimately by honest owners, seems in a fair way to bring about such acute and careful study of the situation that some principles are likely to be formulated for application as a poultice, to draw out what wrong exists and, as far as may be practicable, to heal the difficulties.

That plungers, corruptionists, or adventurers have had to do with the formation of some of the corporations now enjoying special fran-

chises from the public is not a matter for surprise. Nearly all new businesses which promise to grow to great magnitude become the goal of adventurers. It is only after a business has settled into a stable and permanent state, lacking the speculative element, that it becomes generally attractive to men of established business probity, and surely free from the presence or the attacks of speculative adventurers; and the businesses engaged in by most of our public service companies are so new that the price marks still show and the paint is not yet worn. Even the railroads—strong, stable, necessary to the welfare of the country and its civilization as they are—are mere youths. The Rainhill contest, in which George Stephenson publicly proved the preëminence of the steam locomotive over horse flesh or cables for traction, occurred less than eighty years ago, and the railroads of the world are the offspring of that demonstration. The supply of gas for illumination is somewhat older; but the electro-magnetic telegraph as a realized embodiment is only sixty-four years old, and the grandfathers of most of this audience knew naught of such modes of communication. The speaking telephone has extended only through the life of a generation, and it is no more than twenty-five years old as a force in the service of the public. The arc light of the public streets has seen but thirty years of commercial service, and the incandescent electric light has seen even less years in the service of the public. The commercial electric street railway sprang into life less than two decades ago with the success of the Richmond experiment.

In consideration of their tremendous records of development, expansion, and improvement, affording always a great speculative element in their exploitation, it is not to be wondered that projects utilizing these means for serving the public have at times fallen into the hands of speculators or corruptionists. It is useless to waste hard words upon offenders of the past. The duty of good citizenship lies in acknowledging the honesty and squareness which have been manifested in the management of the great proportion of the corporations serving the public, encouraging the right doers, and calmly evolving suitable plans for preventing the recurrence of wrong caused by the intent or the carelessness of those in control of semi-public corporations.

In seeking for such plans, it is obviously necessary to find sound principles upon which to found them. Two bed-rock principles which fit the conditions under which public service corporations do their business are these:

1. The company is granted certain privileges by the public for the purpose of enabling it to furnish readily some type of service to the people, and it should be expected to furnish service fitting the needs of the people; good of its kind, and at prices which are reasonable when judged by the conditions.

The reasons for stating this first of the bed-rock principles in language like the preceding are so obvious and persuasive that I will not delay for the purpose of marshaling them formally before you; and I will turn to make a statement of the second of the two bed-rock principles, in the following words:

2. The company must not be unnecessarily harassed, but must be afforded every reasonable opportunity for economically transacting the business rightfully related to giving the service for which the company was organized; and it must be allowed to make such clear profits over all legitimate costs of its service that it may attract the best and fairest minds to the management, and maintain a position of stable credit with the investing public.

I think the reasons for stating this second principle in this language are also so obvious that the statement will be accepted by most fair-minded and thinking men without argument, but I will stop here to emphasize the significance of certain portions of the statement. In order that the service rendered by a business corporation occupying a special grant from the public may be all that it should be in the details of operation and in its adaptation to the changing needs of the public as public conditions change (perhaps by growing population, greater per capita use of the service, demands that the service be guided into new channels, or those many other causes constantly pressing on the public service corporations), it is of the utmost importance that the operations of the company shall be managed by high-minded, broad-gauge men of foresight and comprehensive grasp of commercial affairs. But such men are ordinarily not attracted to and cannot be retained in the service of companies which are hampered and annoyed in trivial matters, or are put under the pressure of harsh conditions which prevent earning sufficient profits to pay, on the investors' money actually put into the property, returns which the larger merchants and other business men would hold to be reasonable.

Here, however, we begin to get on difficult ground. One of the first difficulties that we meet relates to capital account. To the man who has not been in executive relations with manufacturing or oper-

ating companies, and has not been connected with industrial affairs is natural to assume that the capital invested in a public service pl has been all expended for the labor and material composing the phys property which any one can visually inspect and appraise. Such a is likely to assume, as a matter of course, that every dollar in the value of capital stock or bonds which is not represented by such and material composing the physical property is superfluous, and t fore of the character usually denominated "water." It is a real to such a man, however right-minded he may be, to learn tha view is wrong, and that many expenditures which are outside of and material" are legitimately necessary for the production of an ating plant, and are legitimate charges to capital account.

2. The Legitimate Investment in a Public Service Instal is Greater than the Cost of "Labor and Material" in the Plant

The origination of a project, preliminary surveys and cons plans, and supervising the construction, all cost large sums o in an important project, and this money is wisely expended well-matured plans based on full information (though of large conduce to greater assurance of the project ultimately renderi service at reasonable cost. In other words, it is better to m expenditures out of capital, rather than risk a poorly planned of the project; for experience proves that the latter is likely more cost in the end, and consequently require of the public th of higher prices for service.

Expenditures must also be made for fire, fidelity, an insurance during the time the construction of the plant is u to protect the company from the chance of being wiped disaster of fire or the damage costs due to some unhapp Costly accidents during construction seldom occur in we work, fortunately, but casualty insurance is a wise precauti

Easements for rights of way often cost an electric ligh company considerable sums of money, and the cost of neg such rights, besides the cost of purchasing the rights, prop in capital account.

The cost of organizing the company, the legitimate law due to the work of organizing the project, drawing and

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The well-established public service corporation which is doing its duty, ordinarily should make its charges for service so reasonable that it can pay the investors a return on their invested money which is only enough higher than the ruling rates of interest to make the securities marketable in the face of the precarious, shifting character of a new branch of business which is subject to all of the changes caused by astounding fecundity in discovery and invention. Under these circumstances, the investors are doubtless justified in expecting to receive interest on their money from the moment they pay it in. Where profits are of the speculative character of a mining project, into which money goes with the hope of getting it out many times over, interest for a year or two on the money put in is of relatively small moment; but when the returns are to be governed by normal interest rates, it is proper to expect the interest to start when the investment is made. This being a just and reasonable view, the company ought to provide for interest during the construction of a new project, and as a matter of fact it ordinarily must do so to attract people to invest in its securities, and thus furnish the money to carry out the project.

These items are not all large, but in the aggregate they ordinarily equal a large percentage (generally a number of tens of per cent.), in comparison with the actual cost of labor and material making the physical part of the plant upon which one can directly lay the finger.

Money for all these expenditures must be raised before the completion of the plant. If the expenditures are not charged to the capital account, they must be raised by the creation of a debt to be paid off from operating receipts, which means that early users of the company's products must pay unduly high prices. The fair way is to charge all to the capital account, and let the receipts from service carry the interest on the investment for these items in the same manner as the interest for the investment in brick and mortar, steel and copper is carried. It is therefore unreasonable to criticise a public service company merely because its issued securities have a larger face value than the value of the physical property which may be set down in a schedule, but the situation should be carefully scanned to see whether the difference is beyond legitimate limits before criticism is passed.

The Interstate Commerce Commission enumerates the items pertaining to steam railroads, and belonging in the category to which I am referring, in the following manner in its CLASSIFICATION OF EXPENDITURES FOR ROAD AND EQUIPMENT (that is, the company's investment

upon which interest must be paid), separating them in a somewhat different manner from the way in which I have separated them in the foregoing statements, but including them all as part of the legitimate capital account:

1. ENGINEERING.

To this account should be charged salaries and expenses of all engineers, assistants, and axmen; cost of teams for transportation of engineers and men to and from work, or upon trips of inspection of line of work, or incidental thereto; engineers' instruments, rods, chains, axes, hatchets, tape lines, keel or marking chalk, stakes, profile and drawing paper, tracing linen or paper, cross-section paper, transit and level books, cross-section or topographical books, India ink and colors, drawing boards, stools, map cases, fuel, lights, camp equipage, and other analogous items.

Note.—When employees enumerated above are engaged in work not chargeable to construction, their pay and expenses should be charged to the specific work on which engaged.

2. RIGHT OF WAY AND STATION GROUNDS.

To this account should be charged the . . . salaries and expenses of counsel, right-of-way agent, and engineers and assistants, when specially engaged for such matters; cost of stakes used to denote right-of-way limits; expenses of appraisals, or of juries, commissioners, or arbitrators in condemnation cases; cost of removal of buildings (if upon right of way or station or terminal grounds, and not included in property purchased); commissions paid outside parties for purchase of properties for these purposes; cost of plats, abstracts, notarial fees, recording deeds, etc.; and payments for abutting damages.

Note.—The estimated salable value of property not required in connection with the operation of the road after completion thereof, but acquired and charged to this account in connection with land needed for right of way and station grounds, should, upon completion of the road, be credited to this account and charged to an appropriate property account. Where such property is sold upon or prior to the completion of the road, the proceeds of sale thereof should be credited to this account.

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32. TRANSPORTATION OF MEN AND MATERIAL.

To this account should be charged the fares of laborers and freight charges on material, outfits, and supplies employed in construction work, paid by the railway company and properly chargeable in expenditures for road, but which cannot be correctly charged under any other construction account. This account may include such items as fares of contractors, their walking bosses, paymasters, clerks, and storekeepers; of labor agents; of men hired by labor agencies and shipped out on the line, who may be employed on any character of work; freight on powder, dynamite, and other explosives, hay, grain, groceries, and other supplies for contractors, stores to be sold to sub-contractors, station men, laborers, and others; and other analogous items.

33. RENT OF EQUIPMENT.

To this account should be charged rent, either on the basis of per diem, mileage, or at fixed rates per month, of all equipment (the cost of which is not charged to the line under construction) used in construction of new lines.

34. REPAIRS OF EQUIPMENT.

To this account should be charged repairs and renewals of all equipment used in construction of new lines, not otherwise provided for.

35. EARNINGS AND OPERATING EXPENSES DURING CONSTRUCTION.

To this account should be charged the cost of operating a piece of road while in charge of the construction department and before it is opened for commercial operation. It includes the cost of running construction, material, or other trains when the cost of operating such trains cannot properly be charged to any specific account. To this account should be credited amounts collected for rents of buildings and other properties, and for the transportation of commercial freight or passengers on construction, material, or other trains.

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43. LAW EXPENSES.

To this account should be charged expenditures of the following nature, incurred during the progress of the construction of a road, namely, the pay and expenses of all counsel, solicitors, and attorneys, their clerks and attendants, and expenses of their offices, law books, printing briefs, legal forms, testimony, reports, etc.; fees and retainers for services of attorneys not regular employees of the company; payments to arbitrators for the settlement of disputed questions; costs of suits and payments of special fees, notarial fees, and witness fees; and expenses connected with taking depositions; also all legal and court expenses.

When any of the expenses above enumerated can be charged directly to the account for which incurred, they should be so charged, and not to this account.

(Expenses in connection with condemnation of right of way or station and other grounds should be charged to account Number 2, "Right of Way and Station Grounds," or account Number 3, "Real Estate.")

44. STATIONERY AND PRINTING.

To this account should be charged cost of stationery, stationery supplies, postage, and printing blank books and forms used by all classes of employees in the prosecution of construction work, not otherwise provided for.

45. INSURANCE.

To this account should be charged insurance premiums paid on property of the line under construction and before the road is opened for operation.

Note.—Where insured property is damaged or destroyed, the account to which such property was charged should be credited with the amount of insurance recovered in respect thereof.

46. TAXES.

To this account should be charged state, county, township, city, school, road, and all other taxes and assessments levied and paid on property belonging to the company while under construction and before the road is opened for commercial operation, except special taxes assessed for street and other improvements, such as grading, sewering, curbing, guttering, paving, sidewalks, etc., which should be charged to the account to which the property affected was charged.

47. INTEREST AND COMMISSIONS.

To this account should be charged cash commissions and the actual cash value of other commissions on securities sold; interest, cash commissions, and the actual cash value of other commissions on loans effected and on notes issued for money borrowed for construction purposes or for purchase of equipment; interest on overdue payments to contractors or other creditors; and interest, cash commissions, and the actual cash value of other commissions and exchange on other commercial paper issued for similar purposes. Interest on bonds and other securities, including equipment bonds or car trust notes, paid or accrued during construction and before line is opened for operation, is chargeable to this account. To this account should be credited all interest received on moneys acquired for purposes of purchase or construction of road or equipment.

48. OTHER EXPENDITURES.

To this account should be charged organization expenses, including the payment of all necessary fees; the cost of printing certificates of stock and bonds, with payments to trustees and expenses incurred in the disposal of securities; salaries and expenses of executive and general officers of a road under construction; clerks in general offices engaged on construction accounts or work; rent and repair of general offices when rented, with the furniture and office expenses; also all items of a special and incidental nature which cannot properly be charged to any other account in this classification.

3. EFFECT OF INTEREST ON INVESTMENT ON PUBLIC SERVICE RATES

Interest on the investment has a much larger influence on the rates of a public service corporation than ordinary mercantile experience might lead one to believe. Merchants, bankers, and other business men expect to turn over their capital in every year, and it is not unusual in mercantile business to turn it over several times a year. This reduces the proportion with which the interest on investment enters the prices which must be charged to customers, because the interest is spread over sales aggregating from one to many times the amount of the capital. In most manufacturing branches it is likewise common to turn out annual product of value greater than the capital invested. If the value of product made and sold in a year is twice the amount of the invested capital, it is obvious that 10 per cent. profit on the value of the product,

earned above all manufacturing costs and charges, means 20 per cent. profit on capital.

On the other hand, most public service companies are situated under conditions quite the contrary from those pertaining to the projects of general business and manufacturing. Instead of making a gross annual income equal to or exceeding the capital investment, an electric light company ordinarily must expend a sum of money in establishing its plant and business which is not less than three or four times the annual gross income that it may expect to receive, and which must often be from four to six times the gross annual income. This at once multiplies the influence which interest on capital exerts when charges for service are to be determined, which is exactly the contrary of the conditions which pertain in most of the branches of general business and manufacturing. A public service corporation of this character, therefore, cannot do business on the usual margin of general "manufacturing profit" and live; but a larger proportion of its annual gross income must inevitably be available for meeting the demands of interest, or the project will fail.

4. Good Judgment in Management of Highest Importance

The problem of fixing rates for public utilities falls into even greater difficulties when we come to consider the expenditures during operation. As in the question of the capital account, all expenditures that are illegitimate must be suppressed, but all legitimate and reasonable expenditures which go to improve or cheapen the service and advance the stability of the company must be provided for and allowed. The difficulties here are twofold: First, the difficulty of drawing an exact line between expenditures that should be allowed, and expenditures that are not illegitimate but may not be of sufficient permanent usefulness to the company and its service to justify the expense. Second, the difficulty of determining in what manner and how extensively to provide for various perfectly proper future expenditures that will become necessary to prevent impairment of the capital.

Under the first of these categories come expenditures for several purposes, of which I will name only one which is very often criticised unsparingly, sometimes even in instances where a careful scrutiny would show that the disparagement is unmerited. The expenditures to which I now refer are those for advertising (or pertaining to the

publicity, or new business department, as it is nowadays often called). It is a manifest truth that there can be no reasonable disapproval of advertising that results in a betterment of a company's operating condition so that it can better serve the public or afford its customers lower rates; but determining where this condition ends and a waste of money begins is largely a matter of judgment, and may not be conservatively done.

The ambition to increase the business is one to be encouraged when accompanied by good judgment, and the advertising required to bring about an advantageous increase makes a cost which is undeniably to be encouraged. There are instances, however, in which "publicity" has seemed to become an obsession, and then the cost of advertising has become excessive and has not rendered adequate returns. Obviously, increased business is without advantage for itself alone, so far as the interests of the public are involved, and only that kind of increase should ordinarily be encouraged which brings more satisfactory operating conditions, and therefore improves the service or reduces the cost per unit of service or of product. Advertising which brings returns of that kind, thus paying its own cost and in the end affording advantage to the public, is to be encouraged, however great may be the expenditure; but the kind of publicity which costs more than it brings back to the service, or accomplishes only such temporary results that it makes no profit over its own cost, seems to me to verge on the illegitimate.

Every item in the annual expenses of a public service company which falls in the category to which I am referring should be treated in the manner just applied to advertising. But the difficulty of drawing the line clearly between the right and advantageous and the disadvantageous is almost insuperable. After observing the really marvelous returns which have been obtained from extraordinarily large expenditures for advertising made by certain gas companies and electric light companies, I do not see who is to say in advance, in any particular case, where such expenditures exceed propriety, so long as they are made in a legitimate way. Good judgment combined with caution seem to afford the only guides, and this equally applies to all branches of the operation of a company. Good judgment, then, looms large as an element of the utmost importance in the management of public service companies, if the public is to enjoy low rates and good service; and, honesty and good judgment being established in the saddle, they probably can bring the best results for the public if afforded a large degree of independ-

ence within limits wisely placed by honest legislative bodies. In order that honesty and good judgment may be first established, and then maintained, in the saddle, the full recognition by legislative bodies and commissions of the second principle which I have previously urged is of great importance. Competent men with a combination of the needful fertility, enterprise, integrity, and fidelity cannot be attracted to and permanently attached to projects unless wide scope is afforded for their individual abilities and adequate compensation is made for their services. The possibilities before an able man in general business make it impossible to circumscribe the legitimate opportunities in a public service company and at the same time attract able men to officer the company.

5. Depreciation and Its Allied "Deferred" Accounts

Difficulties of the second order above named, *i. e.*, those relating to provisions for expenditures which will become necessary in the future to prevent impairment of capital, mostly relate to conditions which impose reasons for gradually accumulating a reserve fund from which extraordinary demands for expenditures may be met. Depreciation of plant and the kindred accounts which may be known as "obsolescence" and "required reconstruction" are embraced within these conditions.

A great deal of confusion exists in regard to reserve funds of the kind to which I refer. A public service company which sets aside reserve funds adequate to prevent future impairment of its capital through the depreciation or obsolescence of its plant is often subject to violent attacks by people who are not acquainted with the character of the industries involved. This has led in some instances to a surreptitious treatment of such accounts, which produces a constant temptation to corruption.

There is also confusion in the minds of the people who are in the management of public service companies in respect to the scope of these accounts, and this has sometimes caused abuses in regard to capital charges, sometimes entirely unintentionally.

The technical meaning of depreciation is perfectly well defined. It is well known that any mechanical plant, however well cared for and kept up by current repairs, gradually deteriorates so that it must ultimately be replaced. For instance, a locomotive, kept in the fittest

condition practicable throughout its life, ultimately comes to a point where its general decrepitude puts it beyond the help of rebuilding and repairs, and renders its further use unsafe. It must then be replaced bodily. This gradual deterioration, which constantly goes on and ultimately terminates the useful life of most structures, constitutes depreciation. In the case of a long-established railway system, owning thousands of miles of track, hundreds of locomotives, and tens of thousands of cars, the depreciation may be cared for year by year by each year retiring a suitable number of locomotives and cars and replacing them with new, and rebuilding a suitable proportion of track and other structures each year. In this way the depreciation may be cared for by the expenditure of approximately equal sums of money each year, and the account can be merged with the account for those repairs which are of the current character called "current repairs," and illustrated by the work of the section gangs and the periodical overhauling of locomotives to keep them in economical working condition throughout their useful life.

Few of the other public service companies have reached a magnitude or their art a permanency which enables them to carry the brunt of depreciation in this manner. A telephone company may find it necessary to rebuild an entire line of poles once in ten years, and an electric light company may find it necessary to replace a battery of boilers or an engine-generator set at the end of twenty-five years of useful life. Owning relatively few such units, these companies must treat the expense of such replacements as an extraordinary account, differing from current repairs which can be provided for month by month and year by year at a fairly uniform rate depending upon the business. It is obvious that a company may not be able to meet the extraordinary expense referred to from the income of the particular year in which the replacement becomes necessary, and it is manifestly proper for the company to anticipate and prepare for the situation by accumulating and maintaining a reserve fund which will be sufficient to meet the replacement expenditures as they become necessary. This is the object of the depreciation reserve, or "reserve for reconstruction," as it is called by some, which is commonly maintained by electric light, electric railway, and telephone companies. Its object is manifestly proper, and maintaining such a fund rests on the foundation of honest business judgment.

Two other factors are associated with depreciation in such a manner that they also must be provided for, by most public service companies,

by the accumulation of a reserve fund to meet the extraordinary expenditures which they put upon the company at intervals. These factors relate to the development of the art, which may make an expensive plant obsolete before its natural life is run, and to the reconstruction requirements laid upon the system from time to time by legislation. The first of the factors is commonly referred to as "obsolescence," and it is a factor of much moment in those branches of the business in which the art is changing rapidly on account of fecundity of invention. If a telephone company installs and puts in operation an expensive switchboard and equipment of the most approved type of the day of its installation, but invention shortly thereafter produces apparatus by means of which much more convenient service may be afforded the telephone users, the company is soon forced by the clamor of its customers to substitute the new type of plant for that in use. This is an illustration of obsolescence. The plant in use might have years of natural life before it according to ordinary considerations, but the advance of the art rendered it obsolete; whereupon its replacement was necessary to maintain the business at a satisfactory state. The expense of this replacement might amount to a large part of the company's annual income, or perhaps more than the entire income for one year. It would be unfair to charge the expense of such replacements to the account of capital (bringing in new money for the purpose), as the company has no greater property after the replacement than before, and such a procedure would effectually preclude the possibility of any future reductions of rates to customers or improvements of service; but the proper way to meet the expense of such replacements is to provide a reserve fund, accumulated by annual additions after the manner of the depreciation reserve, and maintained for use when required.

The second of the two factors to which I am now referring differs from obsolescence in form, but possesses like characteristics in operation. I have called it "required reconstruction," for want of a generally adopted term. An electric light company may own a well-built pole line, in excellent condition, which borders a street upon which the city authorities order boulevard improvements, and the wires must go underground. The overhead line had been originally constructed according to good business foresight, as the improvement of this street was not then contemplated; but the required reconstruction involves a large loss on the pole line, because the salvage of material upon its removal is by no means equal to the cost of the construction of the line. A farsighted con-

sideration of the interests of the stockholders of the company, and of the public who are the company's customers, seems to me to call for making good this loss out of a reserve accumulation built up and maintained after the manner of the depreciation reserve. The cost of the new underground construction which replaces the pole line seems to be a proper capital charge, because the company possesses permanent property in that construction and the people living along the improved streets and buying the electric current from the cables may be expected to pay interest on that property. On the other hand, if the old pole line (now removed) is left in capital account, a load is put on future service which may preclude the further and constant improvements in character of service and plant which the public desire, and it seems to the advantage of the public to have the loss which is imposed on the company by the required removal of the pole line made good out of a previously accumulated reserve. The increase in the company's investment on which interest must be secured from the customers, which is caused by the transaction carried out in the manner indicated, is equal to the amount by which the cost of the new underground construction exceeds the then value of the removed pole line, and the sum which must be provided from the reserve fund in carrying out the transaction is equal to the first cost of the pole line diminished by the salvage.

These three factors of depreciation, obsolescence, and required reconstruction may therefore be treated as a unit in the bookkeeping of the company, and a single reserve fund may be accumulated and maintained for their support. As an engineering matter they are separate, but this does not prevent a suitable treatment of them as a unit in the bookkeeping. The commission appointed by the city of Chicago, some two years ago, to study the telephone system in that city, made a careful study of the sum of money which ought to be set aside each year so that the accumulated funds might adequately meet the requirements of these factors as they arise. The report of the commission points out that the annual addition to the accumulated reserve fund ought to average 8 per cent. of the first cost of the plant, including the company's buildings, but not including its land. This 8 per cent. is also separated by the commission into two parts: one, 5¾ per cent., to account for depreciation and obsolescence; and the other, 2¼ per cent., to account for estimated required reconstruction and a small proportion of fire insurance risk which, in this instance, cannot be economically placed with insurance companies. The apparatus of telephone companies is delicate and

fragile, and the telephone art is in a period which is fertile with invention and improvements, which make the rate of depreciation and obsolescence quite large in telephone plants. These factors for electric light, electric railway, and gas light companies are ordinarily counted at a lower rate than the 5¾ per cent. computed by the Chicago Commission for telephone investments in that city.

Some add to these factors an additional one, which they call "inadequacy," which is intended to include a somewhat indefinite expense that may be caused by building a plant piecemeal as the business progresses and develops, instead of all at one time. This manner of building often results in the property units proving too small for the most economical service after the business has gained development, and expense must be incurred for rectifying the error which was essentially due to lack of courageous foresight and understanding of conditions which the future only could expose. It seems to others more reasonable to class expense of this kind as a part of the capital required to develop the business, rather than a factor which may be forecast with some degree of accuracy and cared for out of an accumulated reserve. I will, therefore, here dismiss it without more detailed consideration of its character.

6. The Test of the Equitableness of Rates

My object in dwelling at some length on these details is to bring forcibly to your mind the fact that the normal expenses of operation (including taxes) and the interest on invested money are not the only items involved in a consideration of what constitute equitable rates to be charged for its product or service by a public service corporation, but that reserve funds for reconstruction requirements (and sinking funds needed when the company operates under a fixed term franchise) must be given due consideration. This fact is very often neglected or forgotten in the course of criticism leveled against public service companies. Frank and reasonable criticism will never injure any right-minded corporation, but unjust criticism seldom comes to good. It is natural for the uninitiated to cry out for a large reduction in rates when he learns that the normal expenses of operation of a public service company, such as an electric light company, consume in a particular year (we will say) only 60 per cent. of the total receipts from the customers. An average reduction of the rates by 25 per cent. may appear to him to still leave a goodly margin for the stockholders, but his deductions

are without substance because they are made in neglect of certain important factors which analysis will disclose. I will choose a particular company, for illustration, which has an annual gross income in a certain year equal to substantially one-third of the investment in the property (which is a favorable figure), and for which the average yearly sums set aside for the reserve for depreciation, obsolescence, and required reconstruction ought, according to careful engineering judgment, to amount to not less than 6 per cent. of the invested capital of the company. In this case 18 per cent. of the annual income should go to the reserve to be expended in renewals and reconstruction, or the service will ultimately depreciate and the interests of the customers will suffer in spite of any wishes of the company to the contrary. Sixty per cent. of the annual income is consumed in normal or current expenses of operating (including taxes), and the returns on the capital invested may be made out of the 22 per cent. of the income which remains as a balance. Even if all of this balance is paid to the investors, it does not give to them 22 per cent. on their investment, but only 7⅓ per cent., since the gross annual income is only one-third as great as the invested capital. Seven and one-third per cent. is a large return to expect from mortgage bonds of a great corporation like a railway company, owning some thousands of miles of track and carrying on a profitable business in a diversified territory; but it is small as a return on capital risked in general business or manufacturing, and the average business of the electric light companies, electric railway companies, and the like, partakes of risks resembling those of general business concerns. The obvious deduction is that any reduction in the rates under consideration may be very unwise, because it may cripple the credit of the company, and thereby prevent it from obtaining money to continue a policy of extending its plant and widening the usefulness of its service. Such crippling of a well-managed public service company is likely to curtail the advantages which it can afford its customers (with whom the city itself is generally included, in addition to the large numbers of individual citizens), producing widespread inconvenience to a degree that far more than neutralizes any saving which the customers can make as the result of a small reduction in rates. In the particular instance which I have used for illustration, a reduction of the rates by an average of only 4 per cent. would reduce the margin left for the return on the investment to 6 per cent. of the invested capital, in case the other charges were duly provided for by the company out of its income. This is too narrow a margin

on which to establish the success of an electric light or telephone company, for instance, except in the cases of the largest and most firmly established concerns which enjoy unlimited franchises.

The two bed-rock principles which I named in the early part of this paper seem to me to be equally applicable to the conditions existing in parts of the country which are new and yet to be developed, and in stable and well-settled parts of the country; and the same seems to me to be true of the considerations which I have discussed in association with the two principles. But the deductions cannot be drawn to apply unqualifiedly to all parts of the country. In new parts of the country, the need of the service and the advantages coming as a result of the service may be far in advance of the capital readily available for building plant to render service, and the risks of embarking in projects in an undeveloped region deter investors from furnishing capital unless every reasonable opportunity is opened by the governing authorities for the service company to earn extraordinary returns on the invested capital. The investor who is satisfied with 5 per cent. return per year from an investment of proved permanency may with reason consider 10 per cent. too small to overcome the risks which are united with the earlier years of a public service investment in a new but "hustling" Western city which grants a franchise for a limited term of years. These risks involve many factors which are not found in general business, for a fixed investment in permanent plant must be made from which little salvage can be recovered in case of failure, and success may be accomplished only through shrewd forecasting the character and rapidity with which the city will develop and appraising the stability and personality of its citizens. A manufacturer may ship his product elsewhere, a merchant may move elsewhere with small loss, but a local utility company is rooted to the ground, and the risks surrounding its existence when established in a new though hopefully developing country are correspondingly large. Such a company is also and additionally subject to the chances of ruinous competition, which may be brought on by speculators invading its field in a territory not yet rich enough to support adequately one company, and to the attacks of political and other "strikers" who wish for favors.

This leads me to a third and a fourth basic principle concerning the matter under discussion, which I will state in the following language:

3. A public service company in a new and developing country must see before it opportunity to earn returns on its invested capital which are very large compared with those adequate in stable and thickly settled

regions, in order that it may secure the capital needful for developing its plant and extending its service to meet the apparent needs of an expanding but not yet stable population. If opportunities for honestly earning large returns on the investment in a new country are curtailed by legislation, the development of the service must become inevitably retarded to the disadvantage of the country.

4. A new company, even in a stable country, ought to earn more than current rates of interest for its investors whose enterprise enables them to take the risks of establishing the business, but the rate of return on the investment may be expected finally to approach current rates of interest after the business has become profitable and is firmly established on fixed franchise rights covering a long period.

The fourth principle points to the corollary that the public service companies, well established in the old and permanently settled portions of the country, which have elected to do business under franchises without term limits and are guarded from unjust competition, which conditions now exist in several of our states, must finally expect to give their best grade of service at rates which earn a margin for the investors which is little or no greater than the rate of current interest for tried and sound commercial investments.

The marvelous growth which has hitherto characterized the business of the public service corporations has confined the attention of the officers almost exclusively to the problems connected with the operations of providing service, and has prevented them from giving close attention to the questions involving the relative equitableness of the rates charged for service. In many instances, the condition has resulted in every effort being bent toward the direction of improving and extending equipment and methods of operation, allowing the questions of rates for service to rest entirely on traffic demands and individual judgment applied to specific cases. The books of a large proportion of public corporations do not marshal their data in such a way that the cost of performing service under different conditions can be determined, and the only means for arriving at a basis of rates, then, is that of business expediency or the individual experience of the officials. I think that it may be truthfully said that the latter, applied in a balanced manner, normally tends toward the production of equitable rates, but business expediency applied to individual cases as they arise is likely to lead the other way. However, neither of these methods of fixing rates can be considered either as reasonable or as giving assurance of relative equity in the treatment of customers.

The question of "what the traffic will bear" must always be an element in the determination of rates for public service corporations. This phrase, "what the traffic will bear," has a real significance of great merit, which differs from its popularly accepted meaning of taking all that the customers will give up. According to its correct meaning, it signifies that the charges made for service are adjusted as between the company and each of its customers, so that the company finds the dealings profitable with each, when the full situation is considered, and each customer receives service which as nearly as practicable meets his requirements and costs a price which makes the service advantageous to him, while no unjust discriminations between customers are allowed.

In passing, I will make a note that the last phrase does not involve equal prices to all customers, but does involve the treatment of all customers so that they obtain from the company relatively a full return for their money. An illustration of this statement may be found in considering rates that seem equitable to charge for electric lighting.

In substantially every extended electric lighting project there are a number of consumers who use their electric light for very short periods, occurring only during the hours when the electric lighting plant is carrying its heaviest daily load. The inherent characteristics of the electric lighting business, as we know it, make it impracticable to store commercially large charges of electrical energy, and it is therefore found that loading a plant with this class of service alone makes the cost of the service substantially prohibitive, as all of the interest and depreciation upon the large installation required must be earned from output delivered in short periods each day. The customer who uses current only from five o'clock to six o'clock every week day may cost the company seventy-five dollars per year for fixed charges for every kilowatt in his maximum use (or "maximum demand"), and a rate of twenty-five cents per kilowatt-hour might not be an unreasonable charge to make for his service; while the customer who occupies a dark basement and uses his lights for eight hours per day may cost the company no greater aggregate for fixed charges. Though the latter customer imposes on the company a larger expense for fuel and other operating expenses, the total cost of service to him is relatively smaller, and a price of five or six cents per kilowatt-hour might not be unreasonable to make. If means for storing electrical energy were available of the same convenient cheapness as gas holders for storing gas, the differences would not occur so startlingly. They are more startling in the electric light service than in

the business of most of the other purveyors of public utilities, and the electric light companies have therefore come into the habit of making a sliding scale or "maximum demand" charge for service. The electric railway crowds its passengers into standing room in the cars at the rush periods of the day, and then gives poorer service for the same price as the better service of the normal hours, thus reaching the analogy of a penalty charge for service demanded in the rush hours. This is a condition found in many branches of business. The manufacturer of seasonable goods holds prices stiffly while the demand is large, and makes concessions to close out his stock as the season approaches an end. Retailers do the same. The purchase of a straw hat calls for the payment of a price at the opening of the season which may be one-half larger than the price which will command the same hat two months later. I will not multiply the illustrations. The "maximum demand" charges for electric lighting are based on the existing peculiar conditions of electric lighting and the common experience in commercial affairs, so that the employment of such charges cannot be dismissed as inequitable in spirit, though they result in different rates being paid by different consumers per unit of electrical energy consumed.

The test of equitable charges depends, first, upon their bringing in a total income sufficiently large to pay on the invested capital a return which is reasonable under the conditions of the location, after all normal current expenditures relating to operation are paid and adequately adjusted reserves are provided for. What a reasonable return on the invested capital may be is not a matter that can be fixed once for all or for all locations by dogmatic methods, but it is a matter which must be determined by a consideration of custom and the application of common sense to each instance or class of instances, in a manner analogous to the process by which the common law has developed.

The test of equitable charges depends, second, upon a fair distribution of the charges amongst the various customers, and here again fixed guides are lacking and the dictates of custom and common sense must intervene.

In consideration of the facts to which I have referred, it is plain that the test of equitable charges as between customers does not necessarily reside in all customers of a public service company paying at the same rate per unit for their service, or in the price for a given service being constant at all times. It has also been generally accepted that it does not reside in all customers so paying for their service that each

pays cost plus a fixed percentage for profit. It has been more or less generally accepted that the smaller, short-hour users of electric light should be provided with service at a rate which is within their means, even though the rate may not bear its full proportion of the interest on the investment. It has also been generally accepted that some commodities may with propriety be carried by the railroads at rates which considered alone do not bear their part of the cost of operation plus their full proportion of the interest on investment. But if the touchstone of equitable charges is not found in either of these conditions, where can it be found? This is a question to which the answer is now being diligently sought by public commissions and officers of public service corporations. My own tentative answer to the question is: That the test of the reasonableness or equitableness of the rates maintained by a public service corporation is found in: (1) The effectiveness and simplicity with which the schedule classifies the customers, so that the total required income is collected in a manner which secures the same rate for all customers of a class obtaining approximately like service, though customers belonging in different classes, because they obtain service with differences of character which essentially affect the cost per unit, may be subject to quite different rates; and (2) the certainty with which the rates secure from each class of customers the full annual operating cost of the service in that class and such a proportion of the reasonable return on the investment as the customers' traffic can afford. It then becomes a matter of expediency and public policy to determine whether a company receiving a public grant is justified in taking a larger proportion of profit from one class of customers than from another. This policy has been tacitly approved in the case of steam railroads, which are generally thought to do the entire nation a service by cautiously extending lines into undeveloped territory for the purpose of bringing about its development, though the interest on the investment for the purpose, and even part of the current operating expense, may at first be derived from the income secured by the main stem in older and already developed territory. The policy has also been accepted in a limited degree in electric lighting by the more or less general approval of rates for service to short-hour residence users which in many instances do not bring as large a proportion of profit as the rates applied to some of the longer-hour users, though the latter may pay less for each unit of product or service. The question is a relatively new one, and the ultimate limitations of the policy must rest with experience and the future expressed judgment of our most

judicial minds. It would be a manifest injury to the nation if the policy became so circumscribed that the railroads would feel that equal proportions of profit must be earned on all parts of their systems and from all kinds of traffic. What its effect would be in the case of a corporation giving service within the limits of a single city or a single state is not so clear.

Finally, to apply my criterion of the equitableness of rates requires a more effective organization of their cost keeping than has yet come into vogue with most public service corporations. A few of the companies have adopted their schedule of rates as the result of certain actuarial operations, but most of them have arrived at their schedules by the path of gradual modification through experience; and few can support the reasonableness of their schedules on a foundation of facts produced from their accounting records. I believe that this condition is in a fair way to be overcome. Acute attention is now being given by prominent public service companies of all kinds to studying the cost of service, and the making of improvements in records and in methods of analysis are considered with deep interest. I believe that this is a fortunate state of affairs which will result in the gradual removal of many existing ambiguities in the public service rate question, and will also have an effect in allaying the public suspicion and incredulity which now follow many entirely proper acts of public service corporations.

CONTRIBUTIONS FROM THE
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HYDRATES IN SOLUTION: A REVIEW OF RECENT EXPERIMENTAL AND THEORETICAL CONTRIBUTIONS[1]

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GENERAL PLAN OF THIS REVIEW

DURING the past decade the existence and composition of compounds between solvent and solute in solution has attracted the attention of numerous investigators and resulted in the appearance of a large number of contributions to the problem in recent literature. Since the publication of the monograph of E. Bauer[2] in 1903, however, no systematic treatment of the question has been made.

In view of the widespread interest displayed in this problem, due, no doubt, largely to its important bearing upon the question of solution in general and upon the electrolytic dissociation theory in particular, it has seemed desirable to undertake the collection and systematization of all the recent data bearing upon the question, with the purpose of subjecting the material to a critical treatment. In order to present clearly the principles at the basis of the various methods which have been used in attacking this problem and to evaluate and compare the results with one another, it has been found necessary in many cases (especially in Section I) largely to disregard the conclusions and method of treatment of the individual investigator and to treat his results according to a general plan. Only by some such general system as this is it possible to show the relation of the different methods to one another and to emphasize the relative importance of the results obtained

[1] This review was prepared at the request of the editor of the Jahrbuch d. Rad. u. Elekt., and is published in Heft 4 (1908) of that journal.

[2] Bauer, Ahrens Sammlung, 8, 466 (1903).

by them. It is believed that this mode of treatment will prove of more value than would a simple collection of the results and conclusions of the different investigators. The necessity for some such procedure as this will be appreciated by any one who has occasion to examine the conflicting conclusions of various authors.[3,4,5]

The methods which have been applied to the solution of this problem and the numerous phenomena for which hydration has been offered as the explanation are so varied in character that their division into classes must necessarily be more or less arbitrary. In the following treatment it will be convenient, however, to treat them under three general groupings.

Section I will comprise all methods which depend upon deviations from the laws of the "perfect solution."

Section II will contain the methods which depend upon kinetic conceptions or upon mechanical interpretations of certain phenomena occurring in the solution.

Under Section III will be classed various methods which cannot be classed with the preceding groups.

SECTION I. METHODS DEPENDING UPON VARIATIONS FROM THE LAWS OF THE "PERFECT SOLUTION"

INTRODUCTION

In this group we have the methods which depend upon (1) so-called abnormalities in the effect caused by the solute upon:

(*a*) The lowering of the freezing point of the solvent;

(*b*) The increase in the boiling point of the solvent;

(*c*) The lowering of the vapor pressure of the solvent;

(*d*) The lowering of the solvent power of the solvent;

(2) so-called anomalies in the distribution of a solute between the solvent and a second phase which may be either liquid, gaseous, or

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[3] Compare, for example, some of the conclusions reached by the following investigators: Vaillant, Compt. rend., 141, 659 (1905); Muller and Fuchs, *ibid.*, 140, 1641 (1905);

[4] Magie, Phys. Rev., 25, 172 (1907);

[5] Vaillant, Compt. rend., 138, 1212 (1904); also Bowsfield, R. 90, p. 137, and R. 110, p. 257; and Getman, J. Chim. Phys., 5, 344 (1907).

solid; and (3) variations of the physical properties of solutions from the law of mixtures.

The methods under subdivision (1) of this group are all identical in that they depend upon the measurement of the same quantity in each case, namely, the active mass, or, as I shall here call it, the "activity" (ξ) of the solvent.[6] They are distinguished from one another chiefly by the degree of accuracy attainable in the experimental measurements, by the range of temperature over which they are applicable, and by the ease or difficulty of their thermodynamic treatment. The results obtained by them can, however, in no sense be regarded as independent pieces of evidence supporting the hypothesis of the existence of hydrates in solution, as has sometimes been done. Being simply different methods of measuring the same quantity (the change in the activity of the solvent) they must necessarily lead to the same conclusions as regards hydration.

It will therefore be necessary to consider only one of the methods in detail. The simplest one, and also the best one from almost every standpoint, is the method depending upon the lowering of the vapor pressure. Owing, however, to the historical prominence of the freezing-point method, and because it is the only one which has received any considerable attention at the hands of investigators, it has seemed advisable to consider it in detail, as this is perhaps the best way to illustrate its inferiority, from a theoretical standpoint, when compared with the method depending upon the lowering of the vapor pressure. The researches of Biltz, and especially of H. C. Jones and his co-workers, have yielded a large amount of experimental material of considerable value.

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[6] I use the term "activity" in preference to active mass, which is a misnomer, since it is not the mass but the concentration which is the determining factor in chemical equilibria. The term "activity" has been recently proposed by G. N. Lewis [Proc. Amer. Acad., **43**, 259 (1907); Z. physik. Chem., **61**, 129 (1907)]. It has the same qualitative significance which we are accustomed to attach to the less exact expression "active mass," and in most cases it will be necessary to make use of it in a qualitative sense only, but for some instances where the quantity, ξ, will be used in mathematical equations it is necessary to define it somewhat more exactly. This has been done by Lewis (*loc. cit.*). For the present purpose it will be sufficient to regard the activity, ξ, as a quantity which has the dimensions of concentration; for a perfect gas or ideal solution it is respectively equal to or proportional to the concentration, and for other cases may be regarded as a *corrected concentration*.

An equally exact and general treatment could be given by the use of the thermodynamic potential. This quantity, which has been so fruitful of results in the hands of van der Waals, Planck, van Laar, and others, is, however, unfortunately not yet in general use among chemists, and it has therefore seemed best to use here the more familiar, if less fundamental, conception of "active mass."

The Freezing-Point Method

The assumption of the existence of hydrates in aqueous solution as an explanation of certain anomalies in the freezing-point lowering has been a favorite one with investigators of this phenomenon. Fr. Rüdorff,[7] in 1862, assumed the existence of definite complexes between solute and solvent and attempted to calculate their composition. As the result of his investigation of the freezing-point lowerings produced by a number of salts in aqueous solution, de Coppet[8] found that in many instances the ratio of the freezing-point lowering (C) to the mass of salt (M) in 100 grams of water increased regularly with the concentration. He ascribed[9] this phenomenon to the formation of hydrates and calculated the composition of many of them.

Jones and Chambers,[10] in 1900, continuing some previous work of Jones and Knight,[11] determined the freezing-point lowerings produced by a number of chlorides and bromides, and found that the molecular lowering at first decreased with the concentration, reached a minimum, and then exhibited the regular and continuous increase previously observed by de Coppet. The investigation was later extended to a large number of compounds by Chambers and Frazer,[12] by Jones and Getman,[13] and by Jones and Bassett.[14] The investigation of Biltz,[15] in 1902, along similar lines yielded valuable material. The interpretation placed by these investigators upon their experimental data will be understood from the following considerations.

The equation for freezing-point lowering, Δt, in dilute solution may be written,

$$\frac{\Delta t}{n'} = \frac{k(1+\gamma)}{n}, \qquad (1)$$

[7] Rüdorff, Pogg. Ann., 116, 68 (1862).

[8] de Coppet, Ann. Chim. Phys. [4], 26, 109 (1872).

[9] R. 8, p. 109. "Si les rapports $\frac{C}{M}$ sont *croissant* avec M cela tient à ce que le sel dans les dissolutions a formé au moins une combinaison aux dépens du dissolvant."

[10] Jones and Chambers, Amer. Chem. J., 23, 89 (1900).

[11] Jones and Knight, Amer. Chem. J., 22, 110 (1899).

[12] Chambers and Frazer, Amer. Chem. J., 23, 512 (1900).

[13] Jones and Getman, Z. physik. Chem., 46, 244 (1903).

[14] Jones and Bassett, Amer. Chem. J., 33, 534; 34, 291 (1905).

[15] Biltz, Z. physik. Chem., 40, 185 (1902).

where γ is the degree of ionization and n' the number of mols of solute dissolved in n mols of solvent. If values of the "molecular lowering," $\frac{\Delta t}{n'}$, determined experimentally, be plotted as ordinates against the corresponding values of n' as abscissæ, the curves obtained for electrolytes show distinct minima in most cases. Examples of this are shown in Figure 1, which is taken from the paper of Jones and Bassett (R. 14, p. 536).

The minimum values of $\frac{\Delta t}{n'}$ occur in solutions of moderate concentration, usually between 0.1 and 0.5 molal. In dilute solutions the increase in $\frac{\Delta t}{n'}$ is evidently due to the increase in γ. If the equation is still valid for the more concentrated solutions, the increase in $\frac{\Delta t}{n'}$ can only be due, since γ is decreasing, to a simultaneous decrease in n, which would result if the solute were hydrated and some of the solvent molecules thus removed from their rôle as solvent. A minimum would, therefore, be produced where these two effects neutralize each other, and the distance of this minimum from the axis of the abscissæ would vary inversely with the degree of hydration of the solute for substances of the same ionic type. The magnitude of this depression has been found to be a function of the nature of the ion, so that if the ions are arranged in the order of their effects upon this depression we should obtain the order of their hydration. Beginning with the ion which produces the least effect, the results of Biltz and of Jones and Getman give the following series:

Chlorides, Cs, Rb, K, NH_4, Na, Li.
Chlorides, Ba, Sr, Ca, Zn, Mn, Cu, Ni, Co, Mg, Fe.
Potassium Salts, NO_3, I, Fl, Br, Cl, CN, SCN.

The earlier experiments of Jones and his co-workers led them to the conclusion that hydrates exist only in concentrated solution, breaking down on dilution.[16] It was, however, pointed out by Biltz[17] that Nernst had shown such a conclusion to be directly contrary to the Mass-Action Law and consequently untenable. In his later work Jones has modified

[16] See Chambers and Frazer (R. 12, p. 519), also Jones and Getman, Amer. Chem. J., 31, 355 (1904).

[17] Biltz, Ber. d. chem. Ges., 37, 3036 (1904).

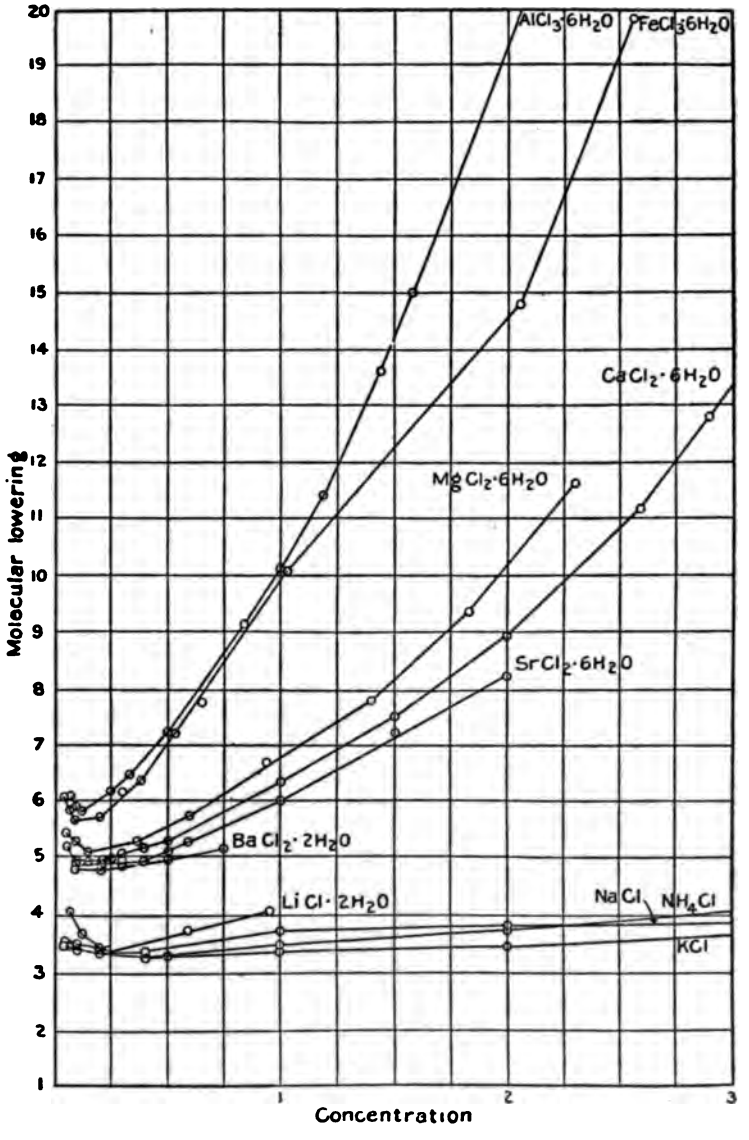
Molecular lowering
Concentration
$AlCl_3 \cdot 6H_2O$
$FeCl_3 \cdot 6H_2O$
$CaCl_2 \cdot 6H_2O$
$MgCl_2 \cdot 6H_2O$
$SrCl_2 \cdot 6H_2O$
$BaCl_2 \cdot 2H_2O$
$LiCl \cdot 2H_2O$
NaCl
NH_4Cl
KCl

FIG. 1

his conclusions so that in most cases they now conform to the Mass-Action Law.[18]

We shall now proceed to examine critically the fundamental assumptions upon which the freezing-point method rests, with particular reference to its availability for the purpose of calculating the approximate composition of the hydrates which exist in solution, a purpose to which it has been extensively applied by H. C. Jones and his co-workers. All such calculations have been based upon the law of Raoult for the lowering of the freezing point, deviations from this law being ascribed to hydration even in the most concentrated solutions.

The law of Raoult for the lowering of the freezing point, like the law of van't Hoff for osmotic pressure, is known to hold, even approximately, only at low concentrations. For an infinitely dilute solution, the former law can be derived rigorously from the latter by means of thermodynamics in the well-known form,

$$\Delta t = \frac{RT_o^2 n'}{\Delta H_o n}, \qquad (2)$$

where R is the gas constant, T_o the freezing point of the solvent on the absolute scale, ΔH_o the molecular heat of fusion of the solvent at its melting point, and n' the number of mols of solute in n mols of solvent. This equation, like that of van't Hoff for osmotic pressure, represents only the limit which is approached as the solution becomes more and more dilute. It results from the general equation, as we shall see later, by omitting certain terms which become negligible as the dilution increases.

It is obvious, therefore, that it is scarcely a justifiable procedure

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[18] It is interesting to note in this connection that Berthelot, in 1879, put forward the theory of the existence of hydrates in solution in order to explain certain irregularities in the specific heats of solutions. As his theory in regard to the nature of these complexes is substantially that which is held today, it seems appropriate to call attention here to his views as stated by him thirty years ago. (The italics are mine.)

"Cette diversité et ces inegalités entre les chaleurs specifiques des dissolutions salines et celles de leurs composants, eau et sel anhydre, paraissent dues, d'après M. Berthelot, à la formation au sein des dissolutions de certains hydrates définis, comparables aux hydrates salins cristallisés; *mais avec cette différence que les hydrates dissous existent le plus souvent au sein de la liqueur dans un état de dissociation partielle, variable avec la quantité d'eau et la température, et suivant des équilibres analogues à ceux des systèmes* éthérés" (*i.e.*, in accordance with the Mass-Action Law. See Mec. Chim. II, 80). [Berthelot, Mecanique Chimique I, 508 (1879)]. Also later, "En résumé, les dissolutions salines doivent être envisagées comme renfermant fréquemment des hydrates salins, tantôt stabiles, tantôt dissociés. Souvent plusieurs de ces hydrates coexistent au sein d'une même liqueur; parfois même ils coexistent avec le sel anhydre, le tout formant un système en équilibre, rigi par les mêmes lois générales que les systèmes homogènes." [Mec. Chim. II, 176.]

to compute the complexity of hydrates in concentrated solutions from the deviations from an equation which strictly represents only the limiting case of the infinitely dilute solution. As an example of the results to which such a calculation has led, a few of the figures obtained by H. C Jones are given below.[19] Jones has applied this equation to the calculation of the approximate composition of the hydrates formed by a large number of substances, both electrolytes and nonelectrolytes, throughout wide ranges of concentration. His calculations in the case of electrolytes also involve the assumption that the degree of ionization is given, at least approximately, by the conductivity ratio. In the following table (Table I) the figures contained in the first three columns are those given by Jones.[20] I have added the last two columns, which follow directly from the content by weight and the specific gravity as given by Jones. It will be noticed from an examination of the figures in the last column that the degree of hydration given by this investigator involves, in all these cases, the "combination" of such a large proportion of the solvent as alone to render the results highly improbable, aside from the fact that the method of calculation is theoretically unjustifiable. When the amount of solvent "combined" amounts in four cases to more than 100 per cent. (as high as 114 per cent. in one instance), it would seem that even this tireless investigator would begin to doubt the validity of his calculations.

TABLE I

Substance.	Mols per liter.	Δt.	Mols of "combined" water per liter of solution.	*Total* mols of water per liter of solution.	Per cent. of water "combined" with solute.
$AlCl_3$	2.0	48.5°	49.08	52.6	93.1
CaI_2	3.1	60.000°	45.8	45.1	101.0
$NiCl_2$	3.5	53.000°	48.9	52.2	93.6
$CuCl_2$	4.4	44.500°	49.77	49.5	100.5
$Cr(NO_3)_3$	1.9	29.500°	44.3	49.1	90.0
H_2SO_4	5.0	76.000°	43.95	43.6	100.8
H_2CrO_4	4.0	57.5°	41.75	36.5	114.0
$C_3H_5(OH)_3$	3.6	36.00°	42.8	45.5	94.0

[19] The work of Jones and his co-workers has been recently collected in a monograph, "Hydrates in Aqueous Solution," Carnegie Inst. Pub. No. 60 (1907).

[20] With the exception of $AlCl_3$, all the values are taken from the above mentioned monograph. The $AlCl_3$ values are from a later publication [Jones and Pearce, Amer. Chem. J., 38, 726 (1907)].

The Fundamental Law of the "Perfect Solution"

Since the law of Raoult for the lowering of the freezing point is applicable only to very dilute solutions, the question naturally arises as to whether there is any general equation for freezing-point lowering which will be valid and give consistent results for solutions of all concentrations. The derivation of such an equation depends upon the law which is to be adopted as the fundamental law for the simplest kind of solution. Such a law must be one which shall be applicable to solutions of all concentrations from zero to infinity. The van't Hoff law for osmotic pressure is obviously not suitable for this purpose, since, as the concentration of a solution increases indefinitely, its osmotic pressure should also increase without limit, a condition which is obviously not consistent with this law.

Now the simplest kind of a solution that can be imagined is a physical mixture in which both constituents exist as simple unpolymerized molecules which do not form complexes with each other. The physical properties of such a solution obey the law of mixtures, being additive with respect to the constituents. A corresponding relation between the activities of the constituents of such a solution is not improbable. Such a relation has been recently proposed by Lewis (see R. 22) as the "criterion of the perfect solution," a perfect solution being by definition one for which this relation holds true. Stated in its most general form, this law is as follows: "At constant temperature and external pressure, the activity, ξ, of each constituent of a perfect solution is proportional to its mol fraction, N, *i.e.*, $\xi = \xi_0 N$ (3), ξ_0 being the activity in the pure state." By the mol fraction, N, is meant the ratio of the number of mols, n, of the substance in question to the total number of mols, $n + n' + n'' + \ldots\ldots$, of all the substances present in the mixture. For solutions whose vapors obey the laws for mixtures of perfect gases, the activity of any constituent is proportional to its partial pressure, and the law may therefore be stated in the following form: "At constant temperature and external pressure, the vapor pressure, p, of each constituent of a perfect solution is proportional to its mol fraction, N."

This form of the law can be readily tested experimentally. The simplest cases of solution met with in practice are those obtained with the liquid hydrocarbons and many of their substitution products. The process of solution in these cases is not attended by any marked heat

effects or volume changes, and the physical properties of the solution are additive with respect to the constituents. The above vapor pressure law has been tested for many of these solutions and *has been found to hold accurately, for both constituents, over all ranges of concentration from zero to infinity.*[21]

All the evidence available, therefore, seems to justify the conclusion that this law is the best one to adopt as the fundamental law of the simplest type of solution. It is obvious that, for solutions in which polymerization, dissociation, or complex formation takes place, deviations from this law are to be expected. By applying it to such solutions we may therefore hope to obtain some light as to the nature and magnitude of the factors which are responsible for these deviations. In the following pages this law and its thermodynamic derivatives will be applied to the data for aqueous solutions and the results interpreted from the point of view of hydration.

The mathematical expression of the law for each constituent of a binary mixture is

$$p = p_o N \quad \text{and} \quad p' = p'_o N' \tag{4}$$

where p and p' are, respectively, the partial vapor pressures of the two constituents from the mixture, p_o and p'_o their corresponding vapor pressures in the pure state, and N and N', respectively, the mol fraction of each or the number of mols of each in one mol of the mixture. Raoult's law for vapor pressure lowering and Henry's law for the solubility of gases are thus special cases of this law.[22]

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[21] Thus this law has been shown to hold for *both constituents* throughout the whole concentration range for the following pairs of substances:

(1) $CO_2 - CH_3Cl$; (2) $C_6H_{14} - C_6H_{18}$; (3) $C_2H_4Cl_2 - C_6H_6$; (3) $C_2H_4Br_2 - C_3H_6Br_2$; (2) $CH_3OH - C_2H_5OH$; (2) $CH_3COOC_2H_5 - C_2H_5COOC_2H_5$; (2) $C_6H_6 - C_6H_5CH_3$; (4) $C_6H_6 - C_6H_5Cl$; (4) $C_6H_6 - C_6H_5Br$; (2) $C_6H_5CH_3 - C_6H_5C_2H_5$; (4) $C_6H_5CH_3 - C_6H_5Cl$; (4) $C_6H_5CH_3 - C_6H_5Br$; (2) $C_6H_5Cl - C_6H_5Br$.

References:

(1) Kuenen, Z. physik. Chem., 11, 38 (1893).
(2) Young, J. Chem. Soc., 81, 768; 83, 68 (1903).
(3) von Zawidski, Z. physik. Chem., 35, 129 (1900).
(4) Linebarger, J. Amer. Chem. Soc., 17, 615, 690 (1895).

[22] This law for the vapor pressures of the constituents of an ideal mixture, and especially the method of expressing concentration in terms of the mol fraction instead of mols per liter, was first used by Willard Gibbs, and has since been consistently used by van der Waals, Duhem, Planck, van Laar, Roozeboom, and others, and is unquestionably the correct method. It has, however, unfortunately not come into general use among chemists, possibly owing to the highly mathematical nature of the treatises of the above writers. See, however, a recent paper by G. N. Lewis, "The Osmotic Pressure of Concentrated Solutions and the Laws of the Perfect Solution" [J. Amer. Chem. Soc., 30, 668 (1908)], where a more detailed discussion of the question will be found than can be given here. See also the numerous recent papers of van Laar, especially, "The Osmotic Pressure of

The vapor pressure, p, of the solvent from the solution can also be written,

$$p = p_o(1 - N'). \qquad (5)$$

Differentiating with respect to N' and substituting for p_o its value, $\frac{p}{1 - N'}$, we obtain the equation,

$$\left(\frac{\partial p}{\partial N'}\right)_T = \frac{-p}{1 - N'}. \qquad (6)$$

This equation expresses the change in the vapor pressure of the solvent from a solution at constant temperature, with the change in the mol fraction of the solute.*

Derivation of the Freezing-Point Formula from the General Law of "Perfect Solutions"

If to a mixture of a solid and its liquid at equilibrium a solute be added which dissolves in the liquid but not in the solid, the temperature of the mixture will fall and the vapor pressures p_s and p of solid and liquid, respectively, will be lowered. The lowering of the vapor pressure of the liquid solvent is due to two effects, namely, to the effect

Solutions of Non-Electrolytes with Reference to the Deviations from the Laws of a Perfect Gas" [Proc. K. Akad. Wet. Amsterdam, 21, 53 (1906)] and "Sechs Vorträge über das Thermodynamische Potential," etc.; "Zwei Vorträge über nichtverdünnte Lösungen und über den Osmotischen Druck" [Braunschweig, Friedrich Vieweg und Sohn 1906], where the thermodynamics of solutions is treated from the standpoint of the Gibbs thermodynamic potential function and the general laws of solutions, both dilute and concentrated, are developed.

* Note added September 10. In a recent publication [Z. physik. Chem., 63, 641, August (1908)], Callendar adopts the equation,

$$\frac{p_o - p}{p_o} = \frac{n'}{n},$$

as the fundamental law for concentrated solutions, n' being the number of mols of solute in n mols of solvent. He applies this equation and its thermodynamic derivatives to the data for aqueous solutions and interprets the results from the point of view of hydration. This equation, however, like the van't Hoff law for osmotic pressure and the Raoult freezing-point equation, must be regarded as strictly applicable only to dilute solutions, its application as a general law for solutions of all concentrations being unjustified. This is readily seen when the equation is written in the form,

$$p = p_o\left(1 - \frac{n'}{n}\right).$$

For a fifty mol per cent. solution, this equation requires that the vapor pressure of the solvent shall be equal to zero and that for higher concentrations it shall be negative.

of the solute and to the lowering of the temperature; or in mathematical terms, if dN' mols of solute be added to 1 mol of a solvent in equilibrium with its solid phase,

$$dp = \left(\frac{\partial p}{\partial N'}\right)_T dN' + \left(\frac{\partial p}{\partial T}\right)_{N'} dT. \tag{7}$$

The change in vapor pressure of the solid is given by the equation,

$$dp_s = \left(\frac{\partial p_s}{\partial T}\right) dT. \tag{8}$$

Since the solid and the solution are kept in equilibrium, $dp = dp_s$, and we have by combining equations (7) and (8),

$$\left(\frac{\partial p_s}{\partial T}\right)_{N'} - \left(\frac{\partial p}{\partial T}\right)_{N'} = \left(\frac{\partial p}{\partial N'}\right)_T \frac{dN'}{dT}. \tag{9}$$

For the influence of temperature on the vapor pressure of a liquid or solid when the total pressure is constant, it can be readily shown[23] that the following equations are rigorously exact.

$$\left(\frac{\partial p_s}{\partial T}\right)_{N'} = \frac{L_s}{VT}, \tag{10}$$

$$\left(\frac{\partial p}{\partial T}\right)_{N'} = \frac{L}{VT}, \tag{11}$$

where L_s and L are respectively the molecular heats of vaporization of solid and liquid under constant pressure, and V is the molecular volume of the vapor at the temperature T. Subtracting these two equations, we obtain,

$$\left(\frac{\partial p_s}{\partial T}\right)_{N'} - \left(\frac{\partial p}{\partial T}\right)_{N'} = \frac{L_s - L}{VT} = \frac{\Delta H}{VT}, \tag{12}$$

where ΔH is the molecular heat of fusion of the solvent into the solution at the temperature T. Substituting this result in equation (9) and combining with (6), we obtain,

$$\frac{dN'}{dT} = \frac{-\Delta H(1 - N')}{PVT}. \tag{13}$$

Substituting $RT = PV$ in (13) and putting $T = T_0 + t$ where T_0 is the absolute temperature of the freezing point of the pure solvent, we have

[23] See Lewis, Proc. Amer. Acad., 37, 53 (1901).

$$\frac{dN'}{dt} = \frac{-\Delta H(1-N')}{R(T_o+t)^2}. \tag{14}$$

In order to integrate, it is only necessary to express ΔH as a function of the temperature.

We shall consider now that we are dealing with water solutions. If ΔH_o is the molecular heat of fusion of ice at 0° and ΔC_p the difference between the molecular heat capacities of ice and water, respectively, at constant pressure, we have the well-known relation,

$$\Delta H_t = \Delta H_o + \Delta C_p t, \tag{15}$$

assuming ΔC_p constant. Making this substitution we have for the final form of the differential equation,

$$\frac{dN'}{dt} = \frac{-(\Delta H_o + \Delta C_p t)(1-N')}{R(T_o+t)^2}. \tag{16}$$

Integrating in the usual manner and evaluating the integration constant by noting that when $N' = 0$, $t = 0$, we obtain,

$$\ln(1-N') = \frac{\Delta C_p}{R} \cdot \ln\frac{(T_o+t)}{T_o} - \frac{\Delta H_o + \Delta C_p t}{R(T_o+t)} + \frac{\Delta H_o}{RT_o}. \tag{17}$$

This form of equation is not convenient to use in practice, however. A simpler form is obtained if the integration is performed by use of Maclaurin's theorem, which can be applied directly to the differential equation, since when $N' = 0$, $t = 0$. Integrating in this manner and retaining only two terms [24] in the series, we obtain

$$N' = \frac{\Delta H_o}{RT_o^2}\left[\Delta t - \frac{1}{2}\left(\frac{\Delta H_o}{RT_o^2} + \frac{\Delta C_p}{\Delta H_o} - \frac{2}{T_o}\right)\Delta t^2\right], \tag{18}$$

where for $-t$ is written Δt, the freezing-point lowering. In the case of water the constants have the following values: [25]

[24] Two terms are sufficient, in the case of water, for all freezing-point lowerings of not more than 7°, assuming an accuracy of 0.001° in the measurements. For lowerings of more than 7° the third term in the expansion should be included.

[25] These values are taken from the most accurate data available. The value of ΔH_o is calculated from the excellent data of A. W. Smith [Phys. Rev., 17, 193 (1903)], using the latest value for the potential of the Standard Clark Cell at 15°, *i.e.*, 1.433 volts [see Guthe, Bull. Bureau Stands., 2, 69 (1906)].

The specific heat of water is taken as 1.0 cal. and that of ice as 0.50 cal. [Bogojawlenski, Chem. Centrbl. II, 946 (1905)]. The value of T_o is that adopted by Buckingham as a result of a careful consideration of all data available [see Bull. Bureau Stands., 2, 273 (1907)]. The value for R is that given by Berthelot [Z. Electrochem., 10, 621 (1904)].

ΔH_o . . .	6009.8	Joules
ΔC_p . . .	36.8	Joules per degree
R . . .	8.3162	Joules per degree
T_o . . .	273.13°	

Substituting these values in equation (18), we obtain for the relation between the mol fraction N' of the solute and the lowering of the freezing point (Δt) in water solution the equation:

$$N' = 0.0096895(\Delta t - 0.00425\Delta t^2) \qquad (19)$$

Application of the Freezing-Point Equation

In order to test this equation for water solutions all the available data on the freezing points of concentrated aqueous solutions of non-electrolytes were collected, and the values of Δt were plotted against the corresponding values of the mol per cent., $100N'$, in each case. The curves for all the substances were plotted on a large scale, together with the theoretical curve. It was found that the experimental curves for the various substances were about equally distributed on both sides of the theoretical curve, and *that, with but few exceptions, all the curves converged into the theoretical curve in the neighborhood of a concentration of 1 mol per liter.*

The complete set of curves on one plot cannot be reproduced without too great a sacrifice of detail, owing to the necessary reduction in size. The points for concentrations from zero up to about twice molal are, however, shown in the accompanying figures. As is evident from these figures, very few accurate data on the freezing points of concentrated aqueous solutions are available. The results of Raoult for ethyl alcohol and those of Raoult and of Ewan for cane sugar are among the few examples of accurate experimental work on concentrated solutions. The heavy line in each figure is the plot of the theoretical equation.

The data on freezing points are by the following observers:[26] Loomis (L), Abegg (A), Jones (J), Roth (R), Raoult (Ra), Ewan (E), Morse and Frazer (M and F).

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[26] Loomis, Z. physik. Chem., 32, 591 (1900); 37, 414 (1901). Abegg, Z. physik. Chem. 15, 218 (1894). Jones, R. 19. Roth, Z. physik. Chem., 43, 560 (1903). Raoult, Z. physik. Chem., 27, 646 (1898). Ewan, Z. physik. Chem., 31, 27 (1899). Morse and Frazer, Amer. Chem. J., 34, 1 (1905); 37, 324, 425, 558; 38, 175 (1907).

Figure 2. — The data for these substances show no systematic variations from the theoretical curve.[27]

Figure 3. — No systematic variations are apparent except perhaps in the case of ethyl formate.[28]

Figure 4. — In the case of the alcohols it is to be noted that the accurate data of Raoult for ethyl alcohol show almost exact agreement with the theoretical curve. The variations in the case of the other alcohols are within the probable experimental errors of the data. In the case of glycerin the three widely deviating points are from the data of Jones and Getman. These results led Jones to conclude that glycerin possesses, to a remarkable degree, the tendency to form hydrates of high molecular weight. These results are, however, probably in error by more than 100 per cent., since the data of the other observers (*i.e.*, Loomis, and Abegg) exhibit no such deviation from the theoretical curve. On the contrary glycerin appears to be quite a normal substance as far as its effect on the freezing point is concerned.[29]

Figure 5. — The data for levulose and dextrose show decided variation from the theoretical, the deviations being such as would be produced if the solute were hydrated.[30]

In connection with the results obtained by Roth for glucose one point is worthy of mention. Roth found that freshly prepared solutions of glucose gave smaller values for the molecular lowering than did the same solutions after standing a few days. The increase in the molecular lowering with the time corresponded to the decrease in the birotation. Hydration has been suggested as a possible explanation of this result, and this is probably the true explanation. A similar slowly progressing hydration, accompanied by a corresponding change in the optical rotation, has been studied in the case of milk sugar and will be discussed later (page 393).

Figure 6. — This shows the data for glycocoll and cane sugar,[30a] both

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[27] Counting from the origin the points are by the following observers: $CO(NH_2)_2$, J. CH_3CONH_2, 1, 2, 4, L; 3, 5, J. $CCl_3COH.H_2O$, 1, 2, 3, 4, 5, 7, 8, 10, R; 11, A; 6, L; 9, 12, J.

[28] CH_3COCH_3, 1, 3, L; 2, A. All others, A.

[29] Points in Figure 4 are: CH_3OH, 1, L; 2, 3, J; 4, 5, A. C_2H_5OH, 1, 3, 4, 6, 7, Ra; 2, L; 5, J. C_3H_7OH, 1, L; 2, 3, J; 4, A.

[30] Levulose, J. Lactose, 1, L; 3, 5, Hudson (see this review, page 393); 4, 6, J. Dextrose, 1, 2, 3, 5, 6, 7, 9, J; 4, 8, 10, R. Mannite, 1, 2, J; 3, L.

[30a] The data for glycocoll are by Roth, and those for sugar by Loomis, Morse and Frazer, Raoult, and Ewan.

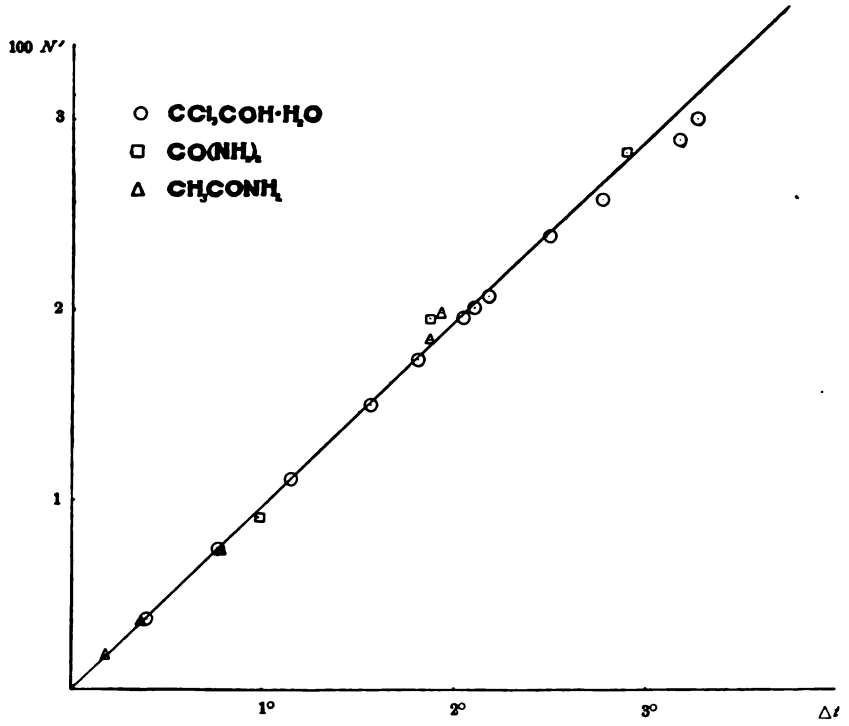
100 N'
3
2
1
○ CCl₃COH·H₂O
□ CO(NH₂)₂
△ CH₃CONH₂
1°
2°
3°
Δt

FIG. 2

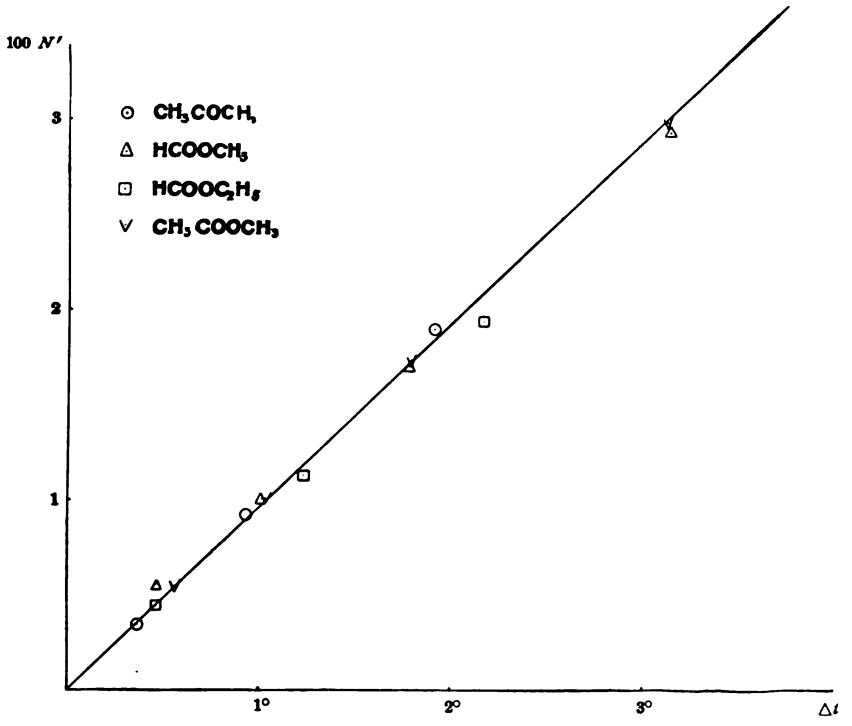
100 N'
3
2
1
⊙ CH₃COCH₃
△ HCOOCH₃
□ HCOOC₂H₅
▽ CH₃COOCH₃
1°
2°
3°
Δt

FIG. 3

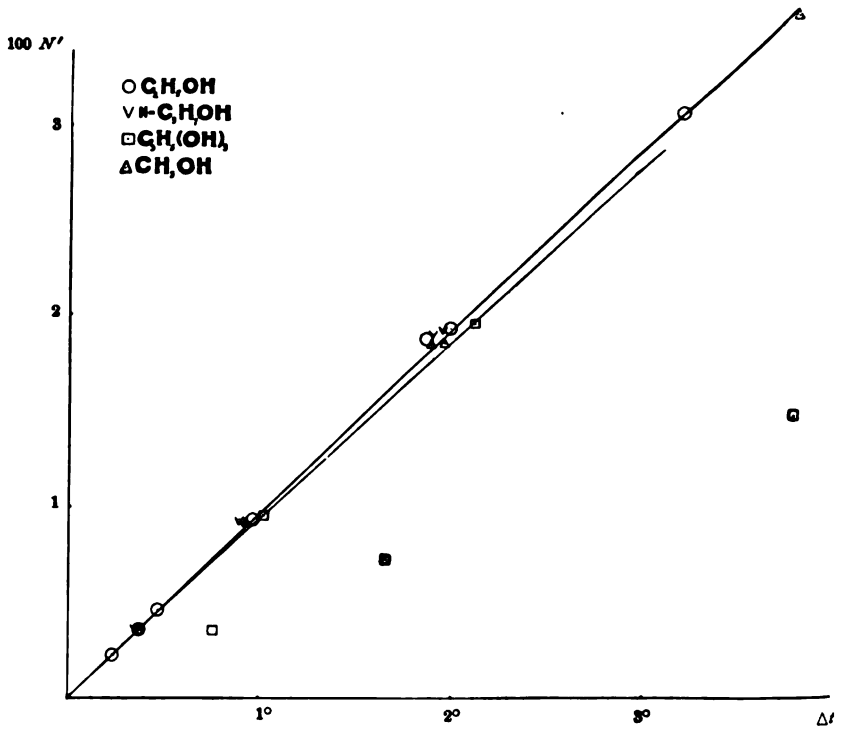
100 N'
○ C_2H_5OH
∨ n-C_3H_7OH
□ $C_3H_5(OH)_3$
△ CH_3OH
3
2
1
1°
2°
3°
Δt

FIG. 4

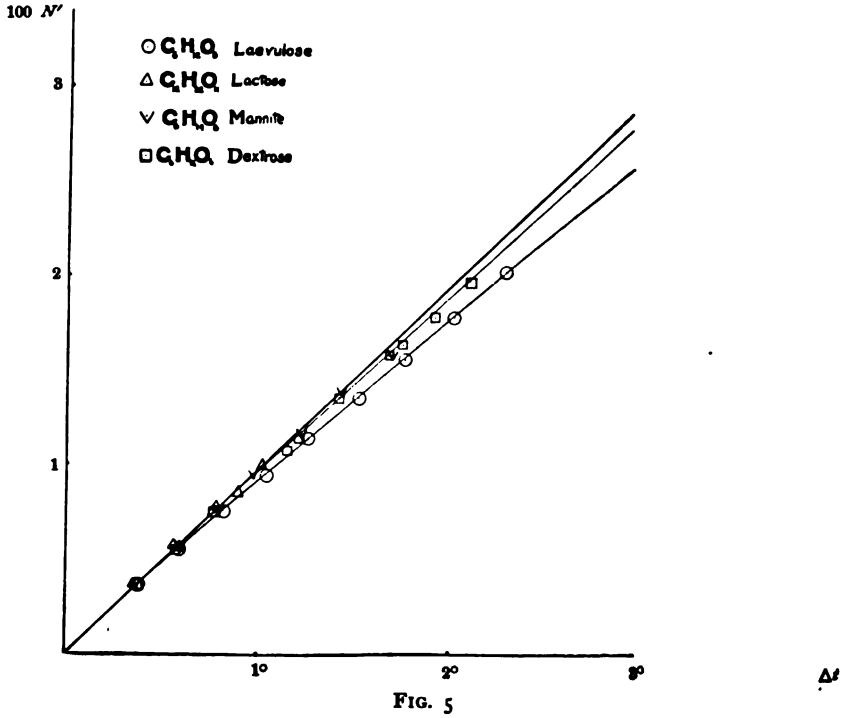
100 N'
○ $C_6H_{12}O_6$ Laevulose
△ $C_{12}H_{22}O_{11}$ Lactose
∨ $C_6H_{14}O_6$ Mannite
□ $C_6H_{12}O_6$ Dextrose
3
2
1
1°
2°
3°
Δt

FIG. 5

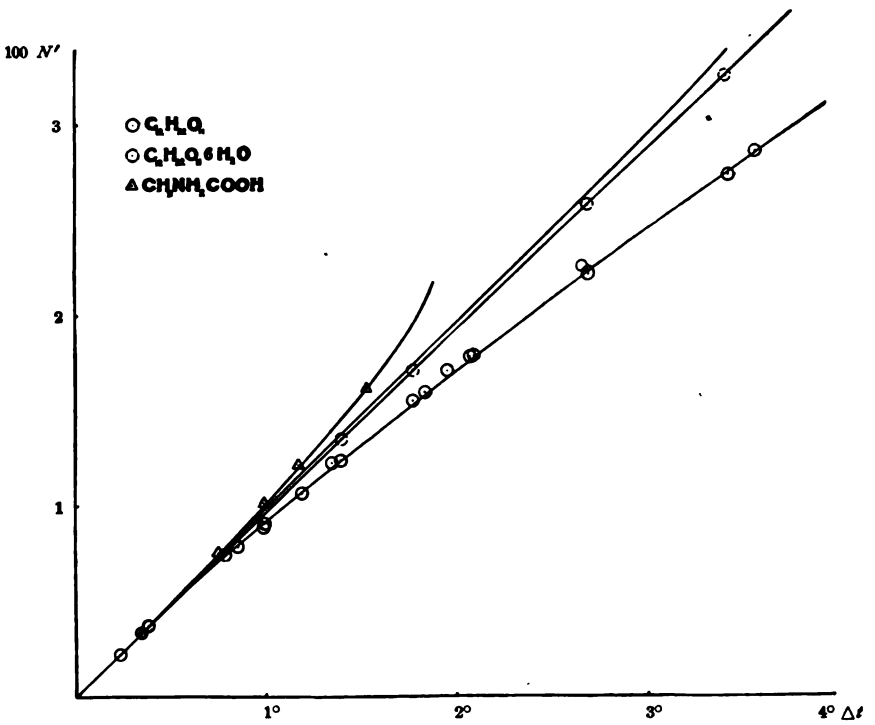

FIG. 6

of which deviate decidedly from the theoretical curve. In the case of the former the deviation is in the direction which would result if the solute were partially associated into double molecules, a result which is more or less to be expected in the case of an amphoteric substance of the nature of amidoacetic acid. The deviation in the case of cane sugar is in the direction which would result from hydration. The dotted circles represent the values obtained for cane sugar if the assumption is made that it exists in solution as the hydrate $C_{12}H_{22}O_{11}\cdot 6H_2O$. This assumption gives values agreeing almost exactly with the theoretical curve. The assumption of the hydrate $C_{12}H_{22}O_{11}\cdot 7H_2O$, on the other hand, gives values lying along the line on the opposite side of the theoretical curve. Beyond twice molal the curve for the hexahydrate begins to deviate again from the theoretical, lying below it.

The foregoing consideration of the freezing-point method shows clearly that if this method is to have any value for the quantitative study of hydration in solution, a formula like that here proposed,

which seems to apply through a considerable range of concentration, to normal, probably anhydrous substances, must be employed, and the application even of this formula must be confined to the region of not too concentrated solutions, say up to twice molal. If this method is to be applied to solutions of electrolytes, the measurements should be confined to solutions preferably in the neighborhood of 0.5 to 0.7 molal, where the degree of ionization as determined by the conductivity ratio may be regarded as at least approximately correct. We are, however, not yet in possession of sufficient accurate data in this region to attempt a quantitative interpretation of the results. If it could be shown that the freezing-point data for some electrolytes (perhaps $CsNO_3$)[30b] fitted the theoretical curve, it would increase greatly the probability that the hydration calculations in the case of the widely deviating ones were somewhere near the truth.

The Boiling-Point Method

The curves showing the relation between the "molecular elevation" of the boiling point and the concentration in mols per 1,000 grams of water exhibit, in many cases, minima similar to those found in the corresponding freezing-point curves, but they are in general much less pronounced.[30c] The relative positions of the minima for different salts with the same anion occur in the same order as the corresponding freezing-point minima, but at greater concentrations in the former than in the latter case. It has been pointed out by Biltz (R. 15, p. 221) and by Jones and Getman (R. 16, p. 343) that this fact would seem to indicate that the complexity of the hydrates in solution decreased with rising temperature, a conclusion which is in accordance with the fact that the complexity of solid crystalline hydrates decreases with rise in temperature. It is also borne out by certain other facts, especially the heats of dilution, as will be pointed out later (page 380).

As in all the other methods of measuring changes in the activity of the solvent, the boiling-point results for concentrated solutions *should not be interpreted by means of a law of the infinitely dilute solution*, as is usually done. By a perfectly analogous method to that used in

[30b] Some results obtained by Biltz (R. 15, p. 218) on the freezing points of some cæsium nitrate solutions indicate that the data for this salt may possibly fit the theoretical curve. A study of freezing points and corresponding conductivities of moderately concentrated solutions of cæsium nitrate will be undertaken shortly by the reviewer.

[30c] See Biltz, R. 15, p. 209; Smits, Z. physik. Chem., 39, 419 (1902); also S. M. Johnson, Trans. Roy. Soc. Ed., 45 [I]. 193 (1907).

deriving the freezing-point formula, a general boiling-point formula for solutions of all concentrations can be derived, based upon the simple assumption that the activities of solute and solvent are proportional to their respective mol fractions. It would, however, unduly lengthen this paper to treat this method in detail, as was done in the case of the freezing-point method. Accurate boiling-point data are, moreover, very rare, a few results obtained by Smits (R. 32, p. 418) being the only ones that I have been able to find which approach the accuracy necessary for a quantitive treatment. The method itself is not as satisfactory either from an experimental or a theoretical standpoint as the vapor-pressure method, which will next be considered.

The Vapor–Pressure Method

Of all the methods of studying hydration in solution, which depend upon changes produced in the activity of the solvent, the method of vapor-pressure lowering is, in general, greatly to be preferred. Being an isothermal method, its thermodynamic treatment is very simple and does not involve the necessity of knowing the values of numerous physical constants, such as the gas constant, heat capacities, heat effects accompanying changes in state, etc., an accurate knowledge of which is necessary in using the equations of the freezing and boiling point methods. It has the further advantage that it can be readily applied over a wide range of temperature and, with proper precautions, it is capable of a high degree of accuracy even at low temperatures. Moreover, the relative degrees of hydration for different concentrations of the solute as calculated from vapor-pressure measurements are directly comparable with one another, since they may all be determined at the same temperature. The results obtained by the freezing-point method, on the other hand, are never directly comparable with one another, since they all correspond to different temperatures, namely, the freezing point of the solution in each case.

This important fact, which seems to have been entirely overlooked by investigators using this method, may well be the explanation of certain results obtained with the strong acids which were apparently contradictory to the Mass-Action Law. The Mass-Action Law requires that the degree of hydration of a given molecular species in solution shall increase with the dilution *at constant temperature*. Jones and Pearce (R. 20, p. 729) found that in the case of the strong acids, HCl,

HNO_3, and H_2SO_4, the freezing-point data seem to indicate that the average molecular hydration of the solute is *increasing* with the concentration. This led these investigators to conclude that hydrates in these cases exist only in concentrated solutions, the assumption being made that only the undissociated molecule possesses the power to form hydrates. This assumption, which was apparently made solely for the purpose of explaining a behavior which it was thought would otherwise constitute a contradiction to the Mass-Action Law, is not at all probable and is not borne out by other facts (R. 100*a*, p. 319). It would indeed not be surprising to find that in the case of the strong acids the degree of hydration *at the freezing point of the solution* should increase with the concentration. These acids possess rather large positive heats of dilution, the greater part of which may well represent heat of hydration; consequently the degree of hydration would increase with falling temperature, and it is therefore rather to be expected that twice molal sulphuric acid, for example, should show a greater average molecular hydration at its freezing point (− 11°) than the molal acid at its freezing point (− 4°), although at constant temperature the change should be in the opposite direction.

In order to render results obtained by the freezing-point method directly comparable with one another, it is necessary to refer them all to the same temperature, preferably 0°. This could be most conveniently done by calculating, thermodynamically, the vapor pressure of each solution at 0° from the observed depression of the freezing point. Such a calculation involves, however, a knowledge of the heat of dilution at 0°, and also possibly of its temperature coefficient if the calculation involved any considerable temperature interval.[81]

The vapor-pressure lowering, Δp, for the perfect solution, is given by the equation,

$$(\Delta p) = p_o N', \qquad (20)$$

[81] Errors due to the failure to appreciate the fact that all results obtained by freezing-point methods refer not to zero degrees but to the freezing point of the solution in each case are not uncommon. Thus Smits [Z. physik. Chem., 39, 424 (1902), and 51, 40 (1905)], using a formula of van Laar's connecting vapor-pressure lowering and freezing-point lowering,

$$\left[\left(\frac{\Delta p}{p_o}\right) + \frac{1}{2}\left(\frac{\Delta p}{p_o}\right)^2 = \Delta t \frac{\Delta H_o}{Rt_o^2} \cdot \frac{T_o}{T}\right],$$

calculates the values of Δp for concentrated solutions from the freezing-point data, and compares them with his own directly measured values at *zero degrees* with "gut Übereinstimmung." Agreement is not to be expected except for solutions with negligible heats of dilution, since the values of Δp obtained by the above formula refer not to zero degrees but to the freezing point of the solution.

which follows directly from equation (4). The application of this equation involves the knowledge of but one constant, p_o, the vapor pressure of pure water at the temperature in question. The necessary data for applying the above equation to water solutions for the purpose of calculating the composition of hydrates are not at present available. The most accurate vapor-pressure measurements in moderately concentrated solutions appear to be those of Smits,[31] all at 0°, which were determined by a differential statical method. He investigated solutions of NaCl, H_2SO_4, KNO_3, and $C_{12}H_{22}O_{11}$. In the case of the first two substances, minima in the values of the molecular lowering of the vapor pressure occur at about 0.5 molal concentration. To illustrate the method of calculating the degree of hydration from vapor-pressure data we will apply the formula to Smits' data for cane sugar at 0°.

We have as the general expression for a perfect solution:

$$\frac{\Delta p}{p_o} = \frac{n'(1+\gamma)}{(1+\gamma)n' + n}. \tag{21}$$

For a nonelectrolyte $\gamma = 0$, and therefore

$$n = \frac{n'p_o}{\Delta p} - n'. \tag{22}$$

For a sugar solution containing 1.0089 mols of sugar per 1,000 grams of water, Smits found $\Delta p = 0.09125$ mm. Assuming $p_o = 4.579$ mm. (Landolt and Börnstein), the above equation gives $n = 49.8$. The total number of mols of water present being $\frac{1000}{18} = 55.5$, the difference, 5.7 mols, represents the average molecular hydration which must be assumed if the deviation from the law of the perfect solution is to be attributed to hydration. This substantial agreement with the value obtained from the freezing-point data, 6.0 mols, is a verification of the experimental data (since neither the difference in temperature nor the heat of dilution is large), but not a theoretically independent confirmation of the conclusion that sugar exists in solution as a hexahydrate.

The Method of Solubility Lowering

The phenomenon of solubility lowering, or the "salting-out" effect, as it is frequently called, has received considerable attention at the hands of investigators, and several theories have been advanced to explain it. We shall confine our attention in the present discussion

to its bearing upon the hydrate problem. Euler[82] has suggested that the "salting-out" effect is to be regarded as a function of the internal pressure (Binnendruck) of the solution. This view is also supported by Geffcken[83] in his critical review of the subject. Rothmund[84] has advanced the hypothesis that the "salting-out" effect is primarily due to a combination between the "salting-out" substance and a portion of the solvent, thereby diminishing the amount of "free" solvent present and hence lowering its solvent power. Levin,[85] however, combats both hypotheses, maintaining that the true explanation is to be found in the mutual action of the two solutes upon each other.

It will be noticed at once that in studying a "salting-out" effect we have always to deal with a ternary system. It is this fact which renders this method so difficult to treat satisfactorily from a thermodynamic standpoint. Accurate differential equations can be set up, it is true, but they cannot in general be integrated. For example, consider a system consisting of N' mols of a solute, s', and N'' mols of a second solute, which we will call for convenience the "salting-out" substance, s'', dissolved in N mols of water, $N' + N'' + N$, being equal to 1. If we increase the number of mols of any constituent, say the substance s'' in the solution, the resulting changes in the activities of all the constituents of the mixture can be shown[86] to be connected by the equation,

$$\left(\frac{N'\partial ln\xi' + N''\partial ln\xi'' + N\partial ln\xi}{\partial N''}\right)_{P,T,} = 0. \qquad (23)$$

This is all that pure thermodynamics will tell us about the changes taking place in such a system. If the solution is saturated with the solute, s', its activity is thereby kept constant and $\partial ln\xi' = 0$, so that the equation becomes

$$\left(\frac{N''\partial ln\xi'' + N\partial ln\xi}{\partial N''}\right)_{P,T,} = 0. \qquad (24)$$

[82] Euler, Z. physik. Chem., 31, 368 (1899).

[83] Geffcken, Z. physik. Chem., 49, 287 (1904). For relations between solubility lowering and other physical properties of solutions, such as compressibility and surface tension, see a recent paper by Ritzel. [Z. physik. Chem., 60, 319 (1907)].

[84] Rothmund, Z. physik. Chem., 33, 413 (1900).

[85] Levin, Z. physik. Chem., 55, 530 (1906).

[86] See Lewis, Proc. Amer. Acad., 55, 530 (1906).

If the concentration of the substance, s'', is sufficiently low, so that the criterion of the perfect solution can be applied to it, we have (see p. 368)

$$\xi'' = \xi''_0 N''.$$

Taking the logarithm of both sides and differentiating, we obtain

$$\partial ln\xi'' = \partial ln N'',$$

which on substitution in equation (24) gives

$$N dln\xi = - dN'',$$

$$\text{or} \quad dln\xi = \frac{d\xi}{\xi} = - \frac{dN''}{N}, \tag{25}$$

an equation first obtained by Lewis (R. 36, p. 279). For the case that the vapor of the solvent obeys Boyle's law, this becomes

$$\frac{dp}{p} = - \frac{dN''}{N},$$

$$\text{or} \quad \left(\frac{\partial p}{\partial N''}\right)_T = - \frac{p}{N},$$

which is identical with equation (6) for a binary system. Stated in words, this means that the addition of a solute to a saturated solution of any substance, s', produces the same lowering in the vapor pressure of the solvent as would be produced if it were added to the same amount of solvent in the pure state.

This conclusion, of course, assumes that no complex formation occurs between the two solutes. Obviously, therefore, so far as the study of the change in the activity of the solvent is concerned, there is no advantage in having the solute, s', present, but rather a disadvantage, since it always introduces the possibility of a mutual action between the two solutes. It is because of this possibility that a three component system is so poorly adapted to the study of the relations between any two of the components. In fact, an examination of the numerous data on the "salting-out" effect shows that, *in general*, the results cannot be explained on the simple assumption of mutual action between solvent and "salting-out" substance. Action between solute and "salting-out" substance also enters to a greater or less degree, depending upon the nature of the two solutes.

Levin (R. 35, p. 528) seems inclined to regard this latter effect as the whole explanation, abandoning the hydrate hypothesis entirely. His

argument, which is also that previously advanced by MacLauchlan,[87] is as follows: "Soll also die Hydrattheorie zur Erklärung der Löslichkeitsbeeinflussung herangezogen werden, so dürfen die in Betracht kommenden Lösungen nicht mehr als, 'verdünnte' gelten. Da aber die hier zur Diskussion herangezogenen Konzentrationen immerhin nicht sehr hohe sind, so scheint es erlaubt, zur Gewinnung eines angenähert richtigen Resultats die Gesetze der verdünnten Lösungen anzuwenden, im besondern das Massenwirkungsgesetz und den von Nernst bewiesenen Satz, dass die aktive Masse des Wassers seinem Dampfdrucke proportional ist. Die einfachste Vorstellung, die man sich von dem Einfluss einer Hydratisierung auf die Löslichkeit bilden kann, ist folgende. Infolge der Hydratbildung der ersten Substanz steht dem zweiten Stoff weniger Lösungsmittel zur Verfügung, seine Löslichkeit sinkt. Nun beträgt die Dampfspannungserniedrigung in normalen Lösungen starker Elektrolyte etwa 4%, um ebensoviel nimmt nach dem Nernstschen Satze die aktive Masse des Wassers ab, während bei gleicher Konzentration die Löslichkeitsbeeinflussung durch starke Elektrolyte im Durchschnitt etwa 20% beträgt. Diese Erklärungsweise ist daher nicht anwendbar, worauf bereits MacLauchlan hingewiesen hat." This argument, however, contains the tacit assumption that the solvent power of a solvent is proportional to its active-mass as measured by its vapor pressure, an assumption which seems scarcely justified.

If the "salting-out" method is to be of any value for the calculation of the complexity of hydrates in solution, the following condition must obviously be fulfilled: the solubility, S, of a solute in a water solution is proportional to the number of mols, N_w, of "free" water which are present in the solution, that is,

$$S = S_o N_w, \tag{26}$$

S_o being its solubility in 1 mol of pure water. Under this assumption the degree of hydration can be calculated for any case from the deviations experimentally found. Unfortunately for the purposes of studying hydration, this assumption is found to be the exception rather than the rule.

A few examples will serve to illustrate the results obtained when this method is applied to the study of hydration. We have already seen (Fig. 2, p. 375) that freezing-point data indicate that chloral

[87] MacLauchlan, Z. physik. Chem., 44, 624 (1903).

hydrate in aqueous solution is a "normal" substance, and therefore presumably not hydrated Its presence in solution in moderate concentration should therefore not affect the solubility of a second solute with which it does not combine in any way. This is, in fact, found to be the case for hydrogen, as shown by the following table, which has been calculated by Philip[38] from the data of Knopp.[39].

TABLE II

Per cent. of chloral hydrate.	c.c. of H_2 dissolved by 100 grams of H_2O.
0.0	18.83
4.91	18.95
7.69	18.92
14.56	18.78
18.77	18.69
29.5	19.07

We have seen (Fig. 6, p. 377) that the freezing-point and vapor-pressure experiments with cane sugar solutions indicate a hydration of about 6 mols of water to 1 of cane sugar. From Steiner's[40] results on the solubility of hydrogen in cane sugar solutions Philip has computed the following table:

TABLE III

Per cent. of sugar.	c.c. of H_2 dissolved by 1,000 grams of H_2O at 15°.	Average molecular hydration of sugar.
0.00	18.83	. .
16.67	17.55	6.5
30.08	16.27	6.0
47.65	13.95	5.4

The figures in the last column show that the presence of each mol of cane sugar in the solution has the same effect on the solubility of hydrogen as would result by the removal of 6 mols of water. So far the results seem to be in complete agreement with those given by the

[38] Philip, Trans. Far. Soc., 3, 141 (1907).

[39] Knopp, Z. physik. Chem., 48, 97 (1904).

[40] Steiner, Wied. Ann., 52, 275 (1894).

previously discussed methods. When we turn to electrolytes, however, the agreement ceases to exist. In the following table are given the results obtained for three electrolytes from the data of Steiner on the solubility of hydrogen in aqueous salt solutions at 15°. From these results it would appear that lithium chloride is the least hydrated of these chlorides, while all other methods unite in giving it the highest hydration.

TABLE IV

Solute.	Mols of salt per 1,000 grams of H_2O.	c.c. of H_2 per 1,000 grams H_2O.	"Average molecular hydration" of the solute.
KCl	0.500	17.30	9.0
	0.956	16.09	8.5
	1.51	14.54	8.4
	2.28	12.54	8.1
	2.65	11.56	8.1
NaCl	0.740	16.20	10.5
	1.75	12.70	10.3
	2.28	10.84	10.3
	3.45	7.80	9.5
LiCl	0.804	16.78	7.5
	1.65	14.78	7.2
	3.18	11.60	6.7

The order in which the "salting-out" power of the various ions increases is, according to Rothmund,

Cations, NH_4, Cs, Li, Rb, K, Na;
Anions, NO_3, I, Br, Cl, SO_4.

This order is approximately independent of the nature of the nonelectrolyte which is being salted out. This fact would indicate that the "salting-out" effect in these cases is due to some action of the "salting-out" substance upon the solvent rather than upon the solute. This conclusion is further strengthened by the fact, first shown by Rothmund,[34] that in many cases the heat of solution of the solute in the salt solution is the same as that in pure water, which would not in general be the case if a reaction occurred between the solute and the "salting-out" substance. It will be noticed that the order of the ions as given above is *not* that obtained from the freezing-point and other data (see

pages 364 and 412), which clearly shows that if hydration is assumed to account for the solubility lowering it is complicated by other effects. Furthermore the above order is not perfectly general, some exceptions being known.

In addition to the above mentioned attempts to calculate hydration from the "salting-out" effect, some recent work of Armstrong[41] and others may be mentioned.[42] Armstrong studied the "salting-out" action of ethyl alcohol and hydrochloric acid on aqueous solutions of the haloid salts of the alkali metals at 25° and calculated the "apparent molecular hydrations" of the two precipitants by the above principle. The results for ethyl alcohol, for example, varied from − .64 to 4.2 mols of water, according to the concentration and the salt which was being salted out. It is scarcely necessary to say that whatever these values may represent they do not represent hydration. Armstrong has also collected all the data on the "salting-out" effect and calculated the "average molecular hydration" of a number of acids, salts, and bases.

In connection with the discussion of this method, the action of salts on the separation of a solution into two phases may be mentioned. Smirnoff[43] has studied this phenomenon in the case of isobutyric acid and water. The method of investigation consisted in determining the temperature at which different amounts of the salt in question caused the solution to become cloudy, owing to the separation of the isobutyric acid. He found that the effect of the cations increased in the series, Cs, Rb, NH_4, K, Na, Li, Cd, Ba, Sr, Ca, Mg, Al, and the anions in the series, NO_3, Br, $\frac{1}{2}SO_4$, Cl. It will be noticed that here the order of the cations is the same as that for their effect on the freezing point, boiling point, etc., as previously discussed[44] (page 364). Smirnoff attributes the result to the hydration of the salts in solution.

Distribution of a Solute between a Solvent and a Second Nonmiscible Phase

This method will, for convenience of treatment, be divided into three divisions, *A*, *B*, and *C*. Under division *A* will be discussed the

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[41] Armstrong, Proc. Roy. Soc., London, 79, 567, 586 (1908).

[42] For a complete list of references to the literature on the "salting-out" effect see R. 33 and R. 35.

[43] Smirnoff, Z. physik. Chem., 58, 667 (1907).

[44] In this connection see also the work of Timmermans on the critical solubility temperatures of ternary mixtures. Z. physik. Chem., 58, 129 (1907).

limiting case where the second nonmiscible phase is the pure solid or liquid solute. This case comprises, therefore, the general phenomenon of solubility of a substance in water and its bearing upon the problem of hydration. Division *B* will deal with a peculiar case of solubility, where the solute exhibits what is called a "maximum rate of solution." The case where the second nonmiscible phase is a liquid or a gas will be treated in division *C*.

A. Solubility-Temperature Curves. — From the general form of the solubility-temperature curves of certain substances in aqueous solution, information regarding the extent of hydration in the solution can

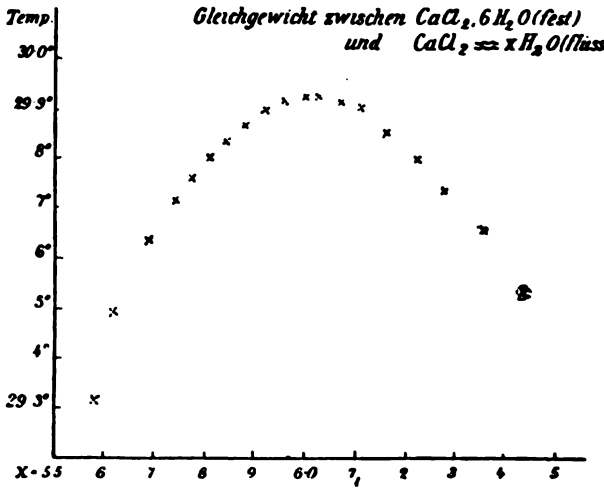

FIG. 7

be obtained. Of especial interest in this respect are the solubility curves of crystalline hydrates, many of which have been investigated. A good illustration of this type of curve is found in the case of $CaCl_2 \cdot 6H_2O$, first investigated by Roozeboom.[45] This curve, which has been carefully determined by Lidbury,[46] is shown in Figure 7. Temperatures are plotted as ordinates, and mols of H_2O per mol of $CaCl_2$ in the liquid phase as abscissæ. As shown by the form of the curve, the solubility of $CaCl_2 \cdot 6H_2O$ in water increases gradually with the temperature, reaching a maximum at 29.92° and then gradually decreasing.

[45] Roozeboom, Z. physik. Chem., 4, 32 (1889).

[46] Lidbury, *ibid.*, 39, 460 (1902).

The first branch of the curve corresponds to a liquid phase containing more, the second branch to one containing less than 6 mols of H_2O per mol of $CaCl_2$. At the vertex the liquid has the same composition as the solid, and this point, therefore, represents the melting point of $CaCl_2 \cdot 6H_2O$.

The effect of the degree of hydration in the liquid phase upon the shape of the solubility curve will be most readily understood by a consideration of the effect of the addition of either $CaCl_2$ or H_2O to the liquid in contact with solid $CaCl_2 \cdot 6H_2O$ at its melting point. Two lim-

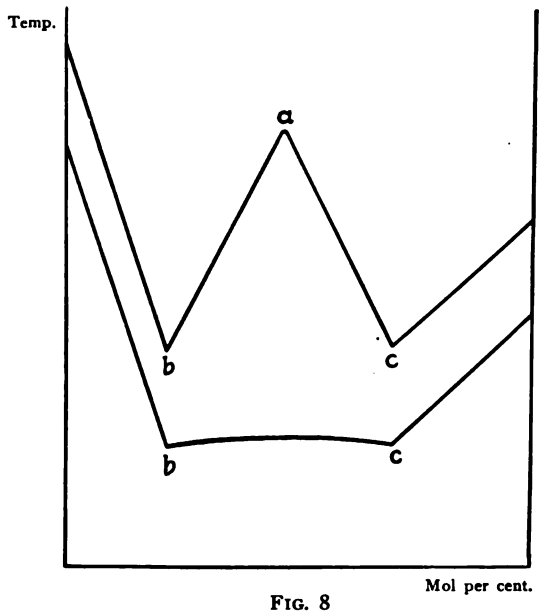

FIG. 8

iting cases are possible: (1) there is almost no dissociation in the liquid phase, hydration being complete; (2) the liquid is practically completely dissociated into $CaCl_2$ and H_2O. In the former case the lowering of the freezing point by the *first* additions of *either* $CaCl_2$ or H_2O to the liquid will be proportional to the number of mols added, and for a perfect solution would be expressed by equation (19) (p. 373). The two curves, one for additions of $CaCl_2$, the other for additions of water, would meet at nearly a sharp angle, and would be approximately straight lines for the first part of their course. Two such curves, *ab* and *ac*, are shown in Figure 8, which represents a melting-point curve

for a "pseudobinary" system, exhibiting a single compound between the two components.

In the second case, where the liquid is highly dissociated, it has been shown theoretically[47] and also experimentally[48] that the first additions of *either* of the products of dissociation, in this case $CaCl_2$ or H_2O, produce no effect upon the freezing point. The curve for this case will therefore be a single straight line or very flat curve, such as *bc* in Figure 8. These two curves represent the limiting cases between which all experimental curves will be found.

As regards hydration in the liquid phase, it can be definitely stated[49] that the mere existence of a solid crystalline hydrate in equilibrium with

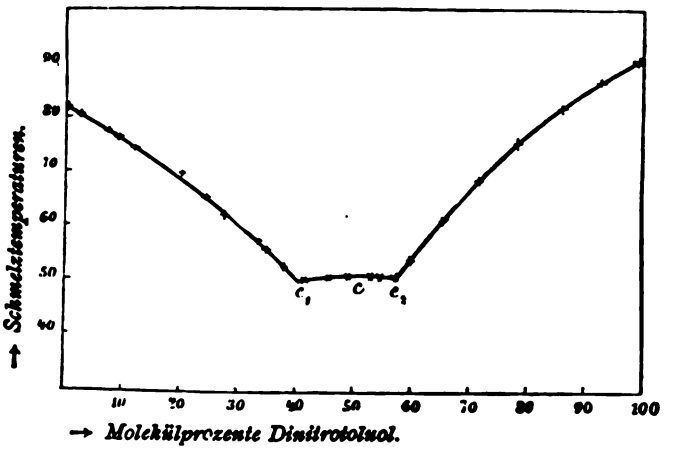

FIG. 9

its solution is proof of the existence of such a compound in the liquid phase; but whether the proportion of it is large or small is not thereby determined. The greater the dissociation in the fused state, the flatter will be the solubility curve at its vertex. The failure of a solid compound to exist in equilibrium with its solution is, however, no indication of the nonexistence of such compounds in the liquid phase. The heptahydrate of sodium sulphate is a familiar example of a crystalline hydrate which is not stable in contact with any aqueous solution of sodium sulphate

[47] Stortenbeker, Z. physik. Chem., 10, 183 (1892); Lewis, R. 6.

[48] Kremann, Monatshefte, 25, 1283 (1904).

[49] Roozeboom and Aten, Z. physik. Chem., 53, 465 (1905).

and whose solubility curve is only realized because of the slow transformation into the stable system. Many such instances are recorded, the most remarkable being the four crystalline hydrates of calcium chromate, none of which is stable in contact with any aqueous solution

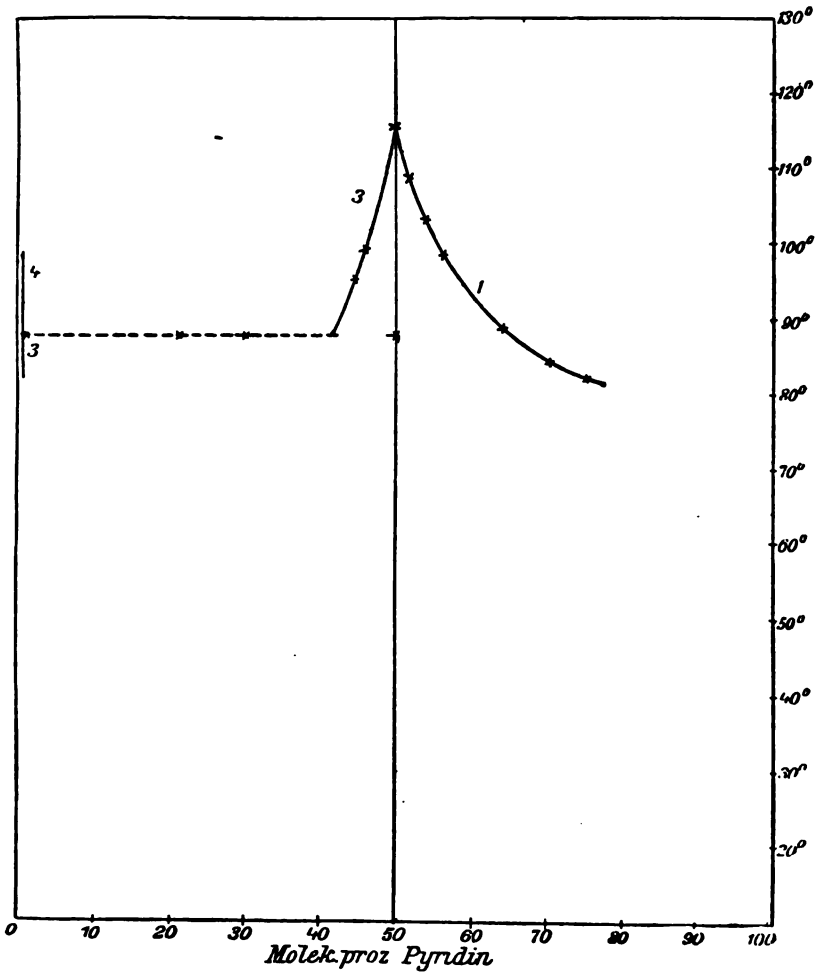

FIG. 10

of calcium chromate. That such hydrates exist in the solution, however, is shown by the fact that they can be precipitated by the addition of other substances, such as alcohol, to the solution.

Two examples taken from recent literature will serve to illustrate the two extreme types of solubility curves for compounds. In Figure 9

for the system dinitro-toluene-naphthalene (R. 48, p. 1283) we have an example of a high degree of dissociation in the liquid state. Figure 10 for the system methyliodide-pyridine[50] illustrates the other extreme, the compound showing little, if any, dissociation in the solution. The solubility curves of most hydrates show the same rounded summit as does $CaCl_2 \cdot 6H_2O$, and are therefore markedly dissociated in the liquid state. Attempts to compute the degree of dissociation from the shape of the solubility curve have been made in some cases.[51] Such calculations in the case of crystalline hydrates especially have little, if any, value, owing to the number of arbitrary assumptions which must be made. The most that can be said is that a rough idea of the dissociation in the liquid state can be obtained by an examination of the solubility curve of a crystalline hydrate.

In dealing with the solubility of one liquid in another, closed curves are obtained in certain cases, an upper and a lower critical temperature being observed. The case of nicotine and water studied by Hudson[52] will serve as an example. Above 210° and below 60° these two liquids are miscible in all proportions. The phenomenon of a closed solubility curve is held to be a characteristic of a ternary system. Thus Dologolenko has recently[53] shown that the closed curve previously obtained for the system water-secondary butyl alcohol is due to the presence of traces of tertiary butyl alcohol. When the perfectly pure secondary alcohol is employed, the lower critical temperature is not observed. In the case of the system nicotine-water, the closed curve, together with a considerable contraction and evolution of heat on mixing, led Hudson to the conclusion that a hydrate was formed in solution, thus making the system a "pseudoternary" one (to follow a nomenclature suggested by Roozeboom) and producing the typical closed curve of such a system. A similar closed curve has been recently obtained by Flaschner and MacEwen[54] for the system water-2-methylpiperidine.

B. Maximum Rate of Solution. — This method for studying the equilibrium between hydrate and anhydride in solution was developed

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[50] Aten, Z. physik. Chem., 54, 127 (1905).

[51] Kremann, R. 48, also Sitzungsber. Wien Akad., 116, 821 (1907); Findlay and Hickmans, J. Chem. Soc., 91, 905 (1907); Van Laar, Kon. Akad. Weten., p. 711 (1906).

[52] Hudson, Z. physik. Chem., 47, 113 (1904).

[53] Dologolenko, Z. physik. Chem., 62, 499 (1908).

[54] Flaschner and MacEwen, J. Chem. Soc., 93, 1000 (1908).

by C. S. Hudson[55] and applied by him to the study of the hydration of milk sugar in solution. Three forms of milk sugar are known, a hydrate, $C_{12}H_{22}O_{11}\cdot H_2O$, and two anhydrides, α and β, of which only the latter is involved in the following considerations.

When a large excess of the solid milk-sugar-hydrate is agitated with water, there is formed in a few minutes a solution whose concentration (called the initial solubility of the hydrate, S_o^H) is independent of the amount of the solid phase present. On continued agitation with water, however, the concentration of milk sugar in the solution increases slowly at a perfectly definite rate, called "the maximum rate of solution" (because it is not exceeded however much solid phase is present), until a final solubility, S_∞^H, is reached. This slow increase in solubility has been shown by Hudson to be due to a slow dehydration of a portion of the dissolved hydrate with the formation of a certain amount of the β anhydride in the solution.

The total increase in solubility, $S_\infty^H - S_o^H$, represents the concentration of β anhydride, which is in equilibrium with S_o^H mols of hydrate. Moreover, the rate of increase in the solubility, S^H, of the solid hydrate is equal to the rate of change of hydrate to anhydride in the solution, *i. e.*,

$$\frac{dS^H}{dt} = \frac{dC_A}{dt} = k_1 S_o^H - k_2 C_A, \tag{27}$$

where S^H is the concentration of the saturated solution at the time t, C_A (equal to $S^H - S_o^H$) is the concentration of the anhydride, and k_1, k_2 are the velocity constants of the two opposing reactions. On integration we obtain the equation,

$$\frac{1}{t} \ln \frac{S_\infty^H - S_o^H}{S_\infty^H - S^H} = k_2. \tag{28}$$

Measurements of the "maximum rate of solution" made at three different temperatures, 0°, 15°, and 25°, gave satisfactory values for k_2 in each case, and the values were found to be related to one another according to the usual equation,

$$\frac{d\ln k_2}{dT} = \frac{A}{T^2}. \tag{29}$$

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[55] J. Amer. Chem. Soc., **26**, 1065 (1904). See also a recent paper by Hudson and Brown, "The Heats of Solution of the Three Forms of Milk Sugar," *ibid.*, 30, 960 (1908).

The separate velocity constants, k_1 and k_2, of the two opposing reactions of hydration and dehydration can be derived from solubility measurements, while from experiments on the rate of change of the optical rotation of freshly prepared milk sugar solutions their sum, $k_1 + k_2$, can be obtained. The two methods were found to give concordant results, so that the phenomenon of mutarotation in the case of milk sugar solutions certainly, and possibly in many other cases, is to be regarded as due to a slow change in the degree of hydration.[56]

The equilibrium constant of the hydration reaction in solution, as determined from the optical rotation, was found to be $\frac{C_A}{C_H} = K = 1.54$ at 20°, while the solubility experiments gave the value,

$$\frac{S^H - S_o^H}{S_o^H} = \frac{C_A}{C_H} = 1.48. \qquad (30)$$

By direct measurements of the equilibrium at different temperatures, and also by calorimetric determinations of the heat of the reaction, Hudson has shown conclusively that the hydration changes but little with the temperature, the change being, however, an *increase* in the degree of hydration with rising temperature. In this respect the reaction differs from most hydration reactions. This fact, together with the slow progress of the reaction at ordinary temperatures and the large change in optical rotatory power which accompanies it ($[\alpha]_D^{20°} = 86.0$ for the hydrate and 35.4° for the anhydride), renders it probable that the hydration is not simply a union of water with the unhydrated molecule to form a loose complex, but that a rearrangement of the atoms within the milk sugar molecule takes place at the same time. The anhydride is the stable form above 94° (the transition point for hydrate and β anhydride). By using the solid β anhydride prepared by crystallization from the solution above 94°, Hudson was able to study the reverse reaction — the slow formation and precipitation of the hydrate at ordinary temperatures — and the results so obtained agreed satisfactorily with the corresponding ones for the direct reaction.

The Vapor Pressures and Freezing Points of Milk Sugar Solutions. — It may be interesting to compare the "average degree of hydration" of milk sugar in solution, as calculated from the variations from the

[56] With reference to other sugars, see the recent paper of Julius Meyer, Z. physik. Chem., 62, 59 (1908). Cf. also Roth's results on glucose, this review, p. 374.

laws of the "perfect solution," with the degree of hydration given by the "maximum rate of solution" method. Hudson[57] has determined the vapor pressures of saturated solutions of the milk sugar hydrate at temperatures ranging from 50° to 100°. For a saturated solution of milk sugar hydrate containing 2.29 mols of $C_{12}H_{22}O_{11}$ per 1,000 grams of water, Hudson found that $\Delta p = 10.8 \pm 0.4$ mm. Hg. The value of p for this temperature is 233.1, whence by substitution in equation (22) the value 3.6 ± 0.8 mols of water is obtained as the average molecular hydration which must be assumed in order to explain the deviation from the theoretical equation on the basis of hydration. Similarly, using Hudson's value, − 0.911°, for the freezing point of a milk sugar solution containing 0.4805 mol of $C_{12}H_{22}O_{11}$ per 1,000 grams of water and applying equation (19), the approximate value, 3 mols of water, is obtained as the average molecular hydration which must be assumed in order to explain the deviation from the theoretical value on the basis of hydration. If this explanation is correct, it requires that in addition to the peculiar and definite monohydrate of milk sugar and the β "anhydride" which exist together in these solutions there must be, also, more complex hydrates of a different character, corresponding more nearly to the usual type of hydrate, their formation not being attended by slowly progressing changes in the rotatory power of the molecule.

The method described in this section is restricted to substances which exhibit a maximum rate of solution, and is therefore not applicable to most electrolytes. Some results obtained by Roozeboom,[58] however, on the solubilities and transition points of the hydrates of thorium sulphate indicate strongly the possibility of the existence of a maximum rate of solution in this instance. He found that solubility measurements of $Th(SO_4)_2 \cdot 9H_2O$ could be made even at 55°, although the transition point of this hydrate into the tetrahydrate occurs at 43°. Similarly, from a saturated solution of the tetrahydrate at 20° the stable nonahydrate precipitated only very slowly even in contact with an excess of solid $Th(SO_4)_2 \cdot 9H_2O$, thus indicating that the change of tetrahydrate into nonahydrate in solution is a slow reaction. The study of the kinetics of this reaction should prove interesting.

C. Variations in the Distribution Ratio of a Solute between Two "Nonmiscible" Phases. — This method of studying complex formation

[57] Hudson, J. Amer. Chem. Soc., 30, 1777 (1908).

[58] Roozeboom, Z. physik. Chem., 5, 208 (1890).

between solvent and solute in solution has been applied by Hantzsch and Sebaldt[59] and by Hantzsch and Vagt.[60] It is based upon the assumption that the distribution of a solute between two nonmiscible solvents, or a solvent and a gaseous phase, is, at least approximately, independent of the temperature, the dilution, and the presence of a second dissolved substance; provided that the solute is a "normal solute," *i. e.*, one which exists in both phases as simple, unpolymerized molecules uncombined with either solute.

In order to appreciate the full significance of this assumption it will be analyzed more closely. When a substance is in distribution equilibrium between two phases, its activity must be the same in both phases, *i. e.*,

$$\xi_1 = \xi_2.$$

For the case that the substance forms a "perfect solution" in the two solvents (or acts also as a perfect gas in case one of the phases is gaseous) we have for a given temperature from equation (3),

$$\frac{N'_1}{1 - N'_1} = k \frac{N'_2}{1 - N'_2}.$$

As the solution becomes very dilute, this relation approaches the equation,

$$\frac{C_1}{C_2} = k,$$

which is Nernst's law for distribution between two solvents, also Henry's law for the solubility of a gas in a liquid.

The assumption that the quotient, k, is independent of the temperature requires that "normal" substances must in general have the same heat of solution in both solvents. Similarly, for the "normal" solute in the "normal" solvent the distribution law should not be affected by dilution or by the addition of a second "normal" solute.

For a series of substances of varied chemical character (*i. e.*, $HgCl_2$, HCN, $C_2H_4(CN)_2$, HCHO, $(CH_3)_2CO$, $CCl_3CH(OH)_2$), Hantzsch found that the distribution ratio between water and a second solvent, such as ether, benzene, chloroform, toluene, etc., was at least approximately constant over a considerable range of temperature. The following examples serve to illustrate this constancy. Concentrations are in mols per liter.

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[59] Hantzsch and Sebaldt, Z. physik. Chem., 30, 258 (1899).

[60] Hantzsch and Vagt, *ibid.*, 38, 705 (1901).

TABLE V

WATER ← CHLORALHYDRATE → ETHER

t.	C_w.	C_{Et}.	$k = \frac{C_w}{C_{Et}}$.
0°	0.178	0.764	0.233
10	0.178	0.764	0.233
20	0.180	0.766	0.235
30	0.180	0.766	0.236

TABLE VI

WATER ← MERCURIC CHLORIDE → TOLUENE, $t = 25°$

C_w.	C_{Tol}.	$k = \frac{C_w}{C_{Tol}}$.
0.2299	0.0201	11.4
0.1149	0.0101	11.4
0.0574	0.0051	11.3
0.0286	0.0026	11.0
0.0143	0.0013	11.0

TABLE VII

WATER ← ETHYLENE CYANIDE → CHLOROFORM, $t = 20°$

Addition.	C_w.	C_C.	$k = \frac{C_w}{C_C}$.
1 mol KOH	0.0790	0.0460	1.71
1 mol KCl	0.0788	0.0462	1.71
1 mol HCl	0.0791	0.0459	1.72

In contrast with these "normal" substances having constant distribution-coefficients, there exist a number of substances for which the distribution ratio varies greatly with the temperature. To this class belong the amines, ammonia, pyridine, bromine, iodine, and carbon dioxide. Variations in the distribution-coefficients are, however, even here, only marked in case one of the solvents is water or a liquid of similar type. Some examples of this type of substances are shown in the following tables. For an electrolyte the distribution law takes the form,

$$\frac{C_1(1-\gamma)}{C_2} = k,$$

where γ is the degree of dissociation in the aqueous solution.

TABLE VIII

WATER ← TRIMETHYLAMINE → TOLUENE

t.	C_w.	C_T.	100γ.	$k=\frac{C_w(1-\gamma_1)}{C_T}$.	$\frac{\Delta k}{\Delta t}$ per cent.
0°	0.0629	0.0084	3.31	7.2	. .
10	0.0582	0.0130	3.45	4.32	4.3
20	0.0535	0.0187	3.60	2.76	2.3
30	0.0477	0 0238	3.80	1.98	1.3
40	0.0417	0.0300	4.10	1.33	0.9
50	0.0360	0.0350	4.40	0.983	0.7
60	0.0322	0.0386	4.70	0.795	0.3
70	0.0270	0.0431	5.10	0.595	0.3
80	0.0233	0.0454	5.45	0.485	0.16
90	0.0225	0.0474	5.55	0.488	0.05
100	. .	. .	. .	[0.420 ext.]	. .

TABLE IX

WATER ← BROMINE → AIR

t.	C_w.	C_A.	$k=\frac{C_w}{C_A}$.	$\frac{\Delta k}{\Delta t}$ per cent.
0°	0.0245	0.00039	63.0	. .
10	0.0219	0.00056	39.0	4.3
20	0.0178	0.00077	23.0	2.8
40	0.0102	0.00095	10.7	0.8
60	0.0058	0.00096	6.0	0.3

TABLE X

WATER ← CARBONDIOXIDE → AIR

t.	C_w.	C_A.	$k=\frac{C_w}{C_A}$.	$\frac{\Delta k}{\Delta t}$ per cent.
0°	0.00805	0.00408	1.97	. .
10	0.00686	0.00496	1.38	4.0
20	0.00468	0.00427	1.11	1.9
40	0.00305	0.00416	0.74	0.8
90	0.00123	0.00327	0.38	0.3

The deviations from the behavior of the "normal" substance exhibited by this last class of substances are such as would result if the solute

in the water layer were hydrated to a greater or less degree. As the temperature is increased these hydrates break down gradually, so that the second solvent should extract more and more of the solute, since the equilibrium between the two layers is an equilibrium between the unhydrated molecules, and increase in temperature increases the proportion of unhydrated molecules in the water layer. This is illustrated by the figures in Tables VIII, IX, and X.[61]

The Physical Properties of Solutions in Relation to the Law of Mixtures

The physical properties of solutions which conform to the so-called law of mixtures are additive with respect to the constituents. This may be expressed mathematically by the equation,

$$X = x'N' + xN, \tag{31}$$

where X is the molecular property in question (*e.g.*, molecular heat, molecular volume, molecular refraction, etc.) and x' and x the corresponding molecular properties of pure solute and solvent, respectively, N' and N being, as before, the mol fractions of solute and solvent, respectively.

In cases where the law of mixtures is not obeyed it is customary to assume, provisionally, that the molecular property of the solvent remains unchanged and to ascribe all deviations from the law of mixtures to changes in the physical property of the solute. This procedure is found, however, in many cases to lead to absurd results for the molecular property of the solute in the solution. To explain these results, it has been assumed that complexes between solute and solvent are formed in the solution. In addition to these purely qualitative conclusions regarding the *existence* of such complexes, numerous attempts have been made to determine their formulæ by means of the positions of certain supposed discontinuities in property-composition curves. (The term property-composition curve will be applied to any curve expressing the change of some physical property of a solution with changes in its percentage composition.) Although the literature[62] contains a large number of

[61] See also Vaubel's [J. prak. Chem., 67, 476 (1903)] measurements on the distribution of the aromatic phenols and amines between water and organic solvents.

[62] For a compilation of the literature on this portion of the subject, see Domke and Bein, Z. anorg. Chem., 43, 125 (1905).

"compounds" of this character, only a few examples will be mentioned in the present discussion, since, probably without exception, the supposed points of discontinuity are due to experimental error. This statement applies even more strongly to compounds whose formulæ have been deduced from the position of supposed points of discontinuity in the first or second differential coefficient of a function connecting some physical property with composition.[63]

Although the existence of points of discontinuity in property-composition curves can be denied, striking irregularities sometimes occur. Some examples of these irregularities will be considered in what follows.

The following physical properties of solutions have, at different times and by various observers, been made the basis for conclusions regarding the existence of hydrates in solution: Heat-capacity, density, viscosity, refractivity, conductivity, compressibility, surface tension, coefficient of expansion, and heat of solution.

Heat-Capacity. — The molecular heat-capacity, C, of a solution whose components are both normal substances would be, according to the law of mixtures [equation (31)],

$$C = c'N' + cN. \tag{32}$$

Mixtures of carbon bisulphide and chloroform are examples of normal liquids which have been shown by Schüller[64] and by Winkelmann[65] to obey this law. Deviations from this law occur in both directions in water solutions. The heat-capacity of water-alcohol mixtures is always greater than that calculated from the law of mixtures, the maximum being reached in a solution containing about 20 per cent. of alcohol.[64]

In the case of most aqueous solutions, however, the heat-capacity of the solution is less than that calculated by the law of mixtures. For these solutions values for the molecular heat-capacity of the solute in the solution have been calculated under the assumption that the molecular heat of the solvent retains the same value which it possesses in the pure state. For most organic solutes the value thus obtained is found to be a constant, independent of the concentration. In the case of

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[63] Pickering, J. Chem. Soc., 51 (1887); 57, 64, 331 (1890). Lupton, Phil. Mag. [5], 31, 418 (1891). Hayes, *ibid.*, 32, 99 (1891). Rücker, *ibid.*, 32, 304 (1892); 33, 204 (1892). Pickering, *ibid.*, 32, 90 (1892); 33, 132, 426 (1892). Chem. News, 63, 305 (1891); 64, 1, 311 (1891). Ber. chem. Ges., 25, 1104 (1892). In this connection see also a recent paper by Lowry, Science Progress, 3, No. 9, 124 (1908).

[64] Schüller, Pogg. Erg., 5, 116, 192 (1871).

[65] Winkelmann, Pogg. Ann., 150, 592 (1873).

nearly all solutions of electrolytes, however, it has been shown by Thomsen [66] that the molecular heat-capacity of the solute in the solution is less than it is in the pure state and that it steadily decreases with dilution, finally passing through zero and becoming negative in dilute solutions.

Since a negative heat-capacity is without meaning, it is obvious that the heat-capacity either of the water as a whole, or a certain portion of it, is lowered by the presence of the solute. To account for this effect, Berthelot,[67] in 1879, assumed the presence of hydrates in the solution, the water in these compounds having a smaller heat-capacity than the uncombined water.

An extended treatment of the heat-capacities of aqueous solutions from this point of view has been recently made by Magie.[68]

Density and Expansion. — According to the law of mixtures the molecular volume, V, of a solution is expressed by the equation,

$$V = v'N' + vN. \tag{33}$$

Numerous examples of substances obeying this law are found among organic compounds, chiefly the hydrocarbons and their substitution products.[69]

If the molecular volume of the solute in the solution be calculated under the assumption that the volume of the solvent is the same as it is in the pure state, it is found that in a few cases (*e.g.*, NH_4Cl, NH_4Br, $LiNO_3$) the value so obtained is greater than the volume of the pure solute. The process of solution in these cases is, therefore, attended by an expansion, the solution occupying a greater volume than the two constituents before mixing. In the vast majority of cases, however, the reverse is the case, the process of solution being accompanied by a contraction. On dilution of a concentrated solution this contraction continues, the molecular volume of the solute in the solution diminishing and approaching a constant value in dilute solution. In a number of cases it even becomes negative, so that the volume of the solution

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[66] Thomsen, Thermochem. Unters., 1, 53.

[67] See note 18, page 366, of this review.

[68] Magie, Proc. Amer. Phil. Soc., 46, 138 (1907); Phys. Rev., 25, 171 (1907).

[69] See a recent paper by Lumsden [J. Chem. Soc., 91, 24 (1907)] in connection with this point.

is less than the original volume of the water used in preparing it.[70] This behavior and its close analogy to the corresponding behavior of

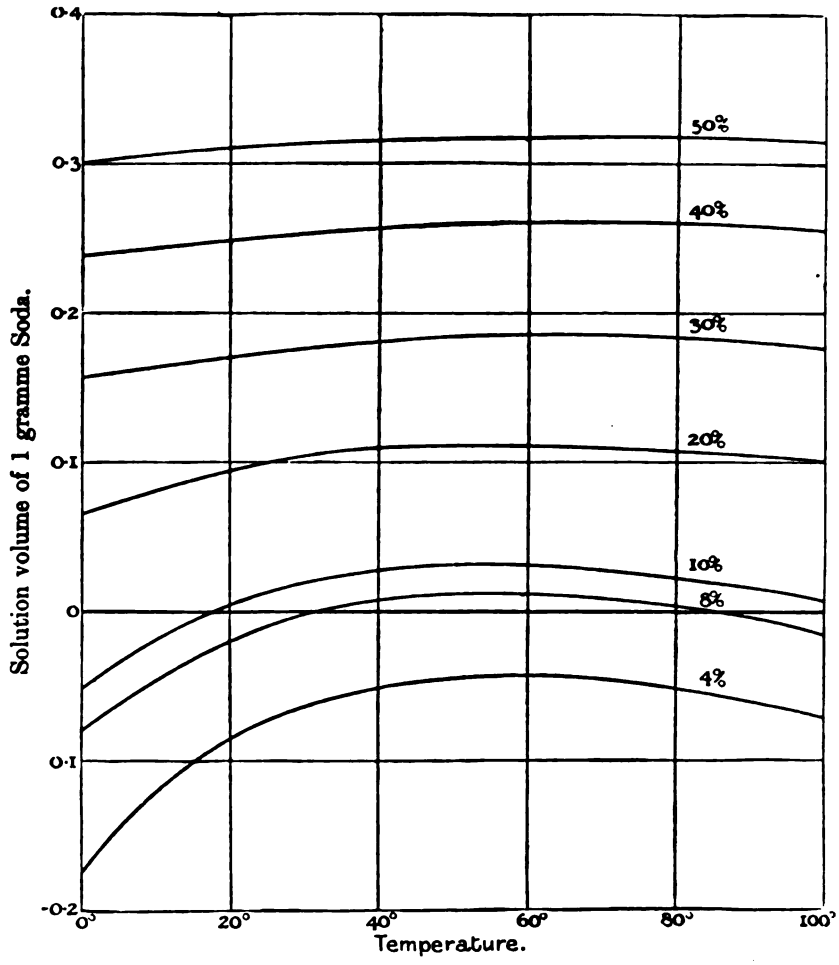

FIG. 11

the heat-capacities as described above were first pointed out by Julius Thomsen.[66]

[70] For example, sulphates of Cd, Co, Cu, Fe, Mg, Ni, and Zn [MacGregor, Trans. Roy. Soc., Canada, 8, Sec. III, 19 (1890); also Pasea, *ibid.*, Sec. III, 27 (1900)]. Hydroxides of Na, Ba, Sr [Carse, Proc. Roy. Soc., Edinburgh, 25, 281 (1904)]. LiOH, Na_2S, Na_2CO_3, NaH_2PO_4, and Na_2AsO_4 [Traube, Z. anorg. Chem., 3, 25 (1893)]. NaOH [Bousfield and Lowry, Phil. Trans. A., 204, 265 (1905)]. For recent tables of the molecular volumes of electrolytes in solution see Ruppin [Z. physik. Chem., 14, 482 (1894)] and Forch [Ann. Phys., 12, 591 (1903)].

A diagram illustrating the volume changes accompanying the dilution of sodium hydroxide solutions at different temperatures is shown in Figure 11, which is taken from the investigation by Bousfield and Lowry.[70] It will be noticed that the volume of the solute in the solution increases with rising temperature and eventually passes through zero and becomes positive for all except the most dilute solutions.

As early as 1872 attempts were made to find relations between the volume of water of crystallization and the density of salt solutions. Owing to insufficient and inaccurate data, these earlier investigators reached the conclusion that crystalline hydrates when dissolved in water dissociated completely into the anhydrous salt and water.[71]

In 1890 Schneider[72] made a careful study of the densities of solid crystalline hydrates and of their aqueous solutions at room temperature. He found that, on the assumption of a constant density for the anhydrous salt, the density of the water of crystallization in solid crystalline hydrates was about 1.2 for a large number of salts. Assuming, accordingly, that the water of crystallization remained attached to the salt when it was dissolved and retained the density 1.2, he calculated the density of the solution according to the law of mixtures and found much better agreement with the observed value than was obtained when this correction was not made. Traube,[73] in 1893, extended these calculations to a larger number of compounds and arrived at the same conclusions, namely, that the density data indicate that salts are hydrated in aqueous solution.

The argument involved here is obviously of the same nature as that used in the heat-capacity method. A negative volume for the solute in solution being impossible, a portion of the solvent, at least, must be denser than the pure solvent. To account for this increase in density it is assumed that a portion of the solvent is combined with the solute, thereby becoming compressed, the assumption being borne out by the increased density of water of crystallization in solid crystalline hydrates.

Turning now to examples of cases where density curves have been used to determine the formulæ of hydrates in solution, we will consider

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[71] Favre and Valson [Compt. rend., 75, 334 (1872); 79, 968, 1037 (1874)]. Southworth [Amer. Jour. Sci., 117, 399 (1879)]. Nichol [Phil. Mag., 16, 121 (1883), 18, 179 (1884); Chem. News, 54, 191 (1886)]. Wanklyn, *et al* [Chem. News, 64, 27, 39, 51, 146 (1891); Phil. Mag., 32, 473 (1891)].

[72] Schneider, Sitzungsber. d. k. Akad. Wien, 99, May (1890); Monatshefte, 11, 166 (1890).

[73] Z. anorg. Chem., 3, 24 (1893).

the solutions of sulphuric and of nitric acids. Owing to the recent investigations of Domke and Bein,[74] of Veley and Manley,[75] of Küster and Kremann,[76] and of Kremann and Ehrlich,[77] we are in possession of considerable data on the physical properties of these solutions.

We will consider first the melting-point diagrams of the two systems in order to find what solid hydrates are known and what is the range of stability of each of them. The diagram (R. 76, p. 22) for the system

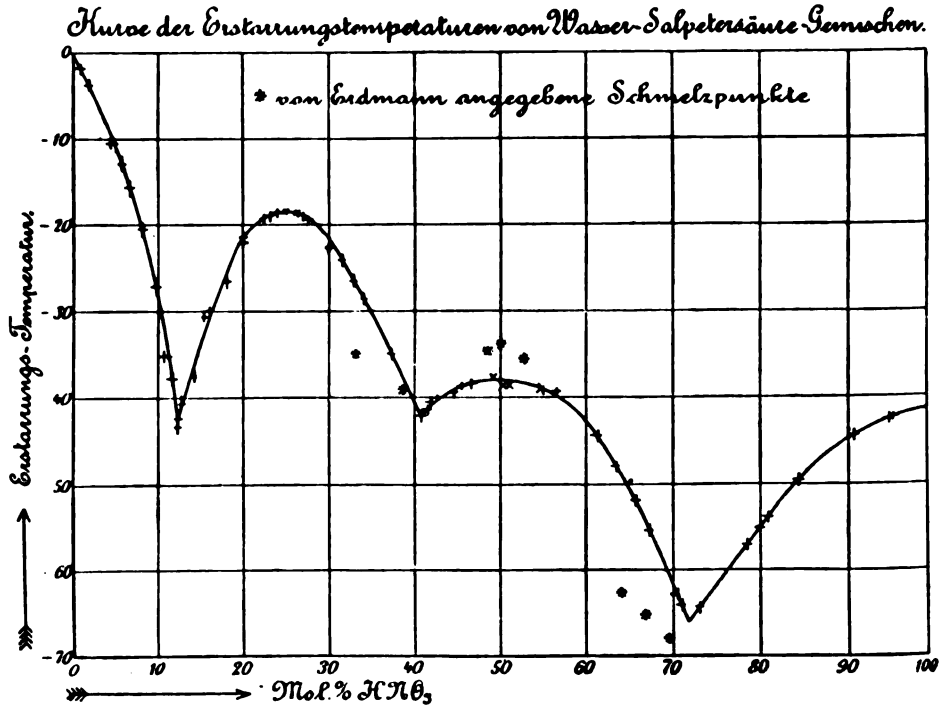

FIG. 12

$HNO_3 - H_2O$ (Fig. 12) shows the existence of two solid hydrates, $HNO_3 \cdot 3H_2O$ and $HNO_3 \cdot H_2O$. Judging from the shapes of the summits of their solubility curves the monohydrate is more dissociated in

[74] Domke and Bein, Wiss. Abhandl. Eich. Komm., 5, 257 (1904).

[75] Veley and Manley, Proc. Roy. Soc., London, 69, 96 (1901).

[76] Küster and Kremann, Z. anorg. Chem., 41, 33 (1904).

[77] Kremann and Ehrlich, Sitz. Wein Akad., 116, 733 (1907).

solution than the trihydrate. The melting-point diagram[78] for the system $SO_3 - H_2O$ (Fig. 13) shows the existence of three solid hydrates of sulphuric acid, viz., $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, and $H_2SO_4 \cdot 4H_2O$, only the first one being capable of existence above $-15°$, however.

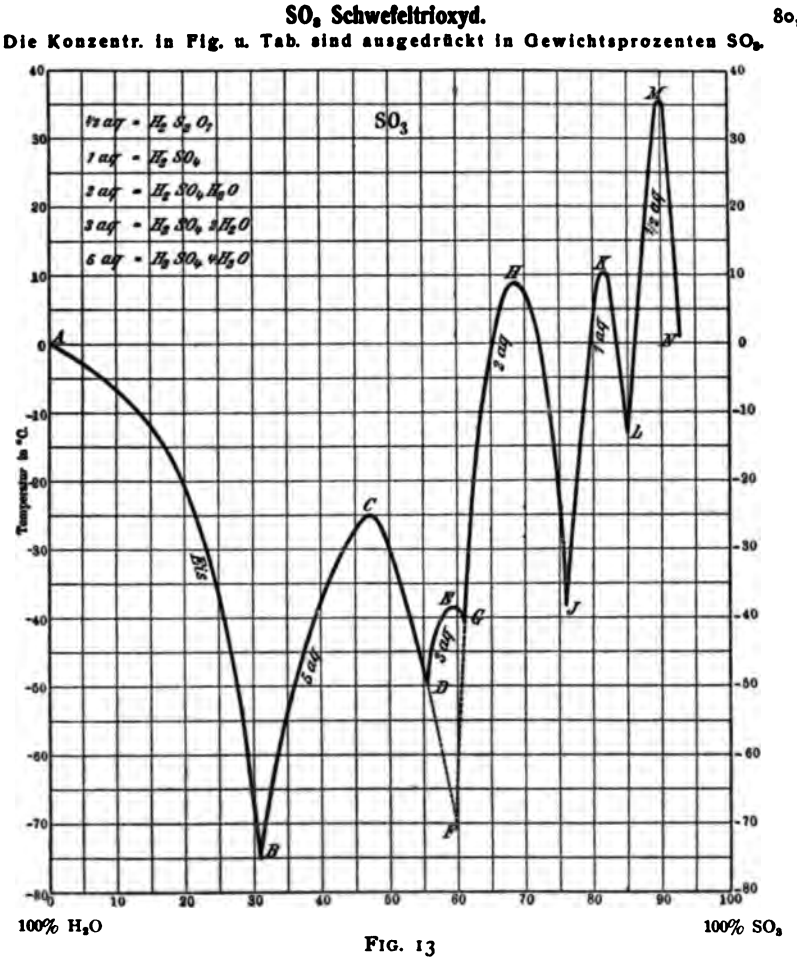

FIG. 13

In the curve showing the relation between the density and composition of nitric acid solutions, Veley and Manley (R. 75, p. 119) found that points of discontinuity occurred at "points corresponding to the

[78] This diagram, prepared by Meyerhoffer from all existing data, is on page 567 of the last edition of Landolt and Börnstein.

composition of hydrates of HNO_3 with 14, 7, 4, 3, 1.5, and 1 molecule of water, respectively."

These points of discontinuity must, however, be regarded as due to experimental errors. Domke and Bein, in their exhaustive investigation of sulphuric acid solutions, have shown most clearly and conclusively that breaks of this kind do not occur in density curves and that no reliable results concerning the formulæ of hydrates can be drawn from density curves. The matter is aptly stated by Küster and Kremann (R. 76, p. 31) as follows: "Ein beliebtes und deshalb häufig, aber meist ohne die erforderliche Kritik angewendetes Verfahren, 'Hydrate' in Lösungen verdünnter Sauren nachzuweisen ist die Ermittelung der

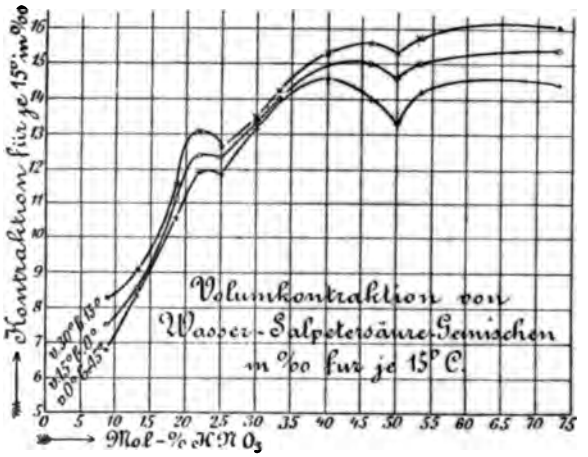

FIG. 14

Volumgewichte, 'Knicke,' and zwar in der Regel mit grosser Kunst and gelinder Gewalt in den Volumgewichtskurven aufgefundene 'Knicke,' zeigen dann so viel 'Hydrate' an, als der Geduld des Experimentators entsprechen. Diese Methode ist auch von Veley schon vor einigen Jahren mit bestem Erfolg bei der Salpetersaure angewendet worden."

These investigators accordingly studied the expansion coefficients of nitric acid solutions and discovered irregularities in the neighborhood of compositions corresponding to the hydrates $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$, which they attributed to the presence of these compounds in the solution. Their results are shown in Figure 14. Contractions (expressed in parts per thousand) for temperature changes of 15° at different intervals are plotted as ordinates and mol per cent. of HNO_3 as abscissæ.

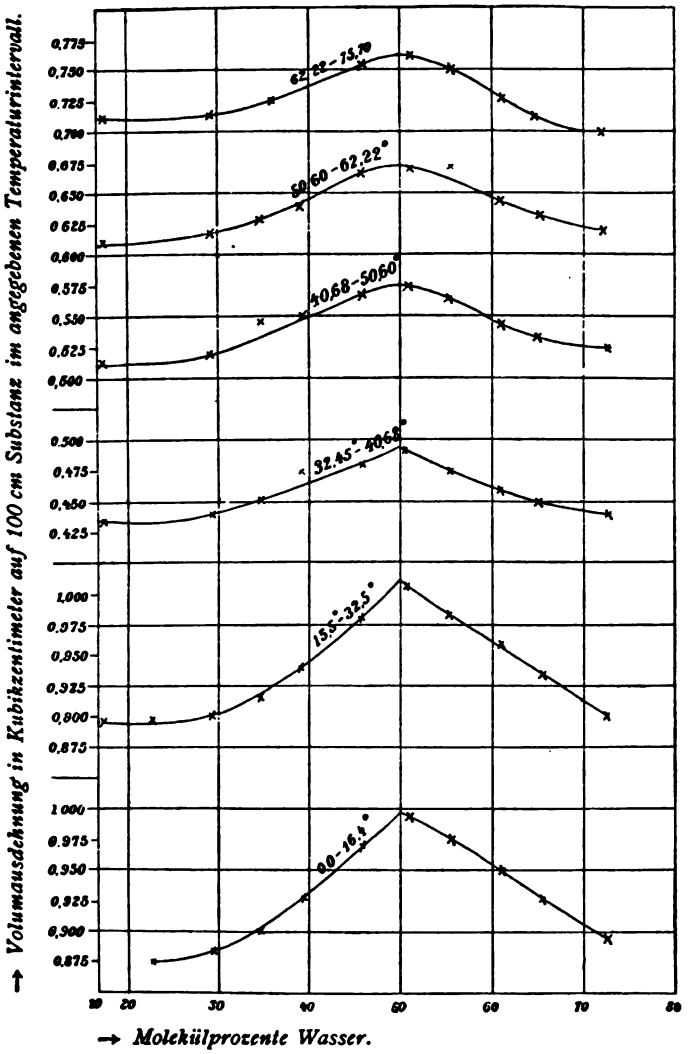

FIG. 15

A similar set of curves[79] for the system $H_2SO_4 - H_2O$ is shown in Figure 15. The curves at the lower temperatures show an irregularity[80] in the neighborhood of the composition corresponding to the hydrate

[79] From Kremann and Ehrlich, R. 77, p. 749.

[80] None of these irregularities should be represented as points as they are shown in these figures and also in Figure 17, since abrupt changes cannot occur in such curves. The irregularities represent only maxima and minima.

$H_2SO_4 \cdot H_2O$. No irregularities appear, however, in the neighborhood of compositions corresponding to the di- and tetra-hydrates, whose solubility curves are shown in Figure 13. The irregularity is seen to become less and less distinct as the temperature rises, which the authors attribute to the gradual dissociation of the monohydrate into its constituents. For the system aniline-nitrobenzene, which do not form any compound with each other, these investigators showed the absence of any such irregularities and of any decided temperature effect.

Viscosity. — According to Dunstan [81] the viscosity curves of mixtures fall into three classes: (1) Curves which obey the law of mixtures; (2) curves displaying minima; (3) curves displaying maxima. In case of curves displaying minima, according to Dunstan, the process of solution is accompanied by a decomposition of associated into simple molecules. The presence of maxima is attributed to the formation of complexes between the constituents. Numerous examples of each type will be found in the papers of Dunstan and his co-workers, also in recent papers by Tsakalotos,[82] Getman,[83] Kremann and Ehrlich,[77] and Beck and Ebbinghaus.[84]

As in the case of the density curves, we find mentioned in the literature numerous hydrates whose formulæ have been deduced from the positions of certain supposed points of discontinuity in viscosity curves belonging to the third type. Thus for the system $CH_3OH - H_2O$ we have, according to Varenne and Godefroy,[85] hydrates containing 1, 2, 3, 5, 8, and 20 molecules of water, respectively, but according to Dunstan [86] only the di- and tri-hydrates. Similarly, four hydrates of acetone [87] and seven of ethyl alcohol [88] have been announced recently, based upon the same evidence.

That these points of discontinuity in the viscosity curves of methyl-

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[81] Dunstan, Z. physik. Chem., **49**, 590 (1904); **51**, 732 (1905); **56**, 370 (1906). Trans. Chem. Soc., **85**, 817 (1904); **91**, 83 (1907).

[82] Tsakalotos, Bull. Soc. Chim. (4), **3**, 224, 242 (1908).

[83] Getman, J. Chim. Phys., **4**, 386 (1906).

[84] Beck and Ebbinghaus, Z. physik. Chem., **58**, 436 (1907).

[85] Varenne and Godefroy, Compt. rend., **138**, 990 (1904).

[86] Dunstan, Z. physik. Chem., **49**, 595 (1903).

[87] Varenne and Godefroy, R. 85, p. 992.

[88] Varenne and Godefroy, Compt. rend., **137**, 993 (1903); Dunstan, R. **86**, p. 593; Gaillard, J. chim. Pharm., **6–26**, 481 (1907).

alcohol-water mixtures are purely imaginary and due to experimental errors will be evident from an examination of Figure 16, which contains Getman's viscosity curves (R. 83, p. 391) for this system at a

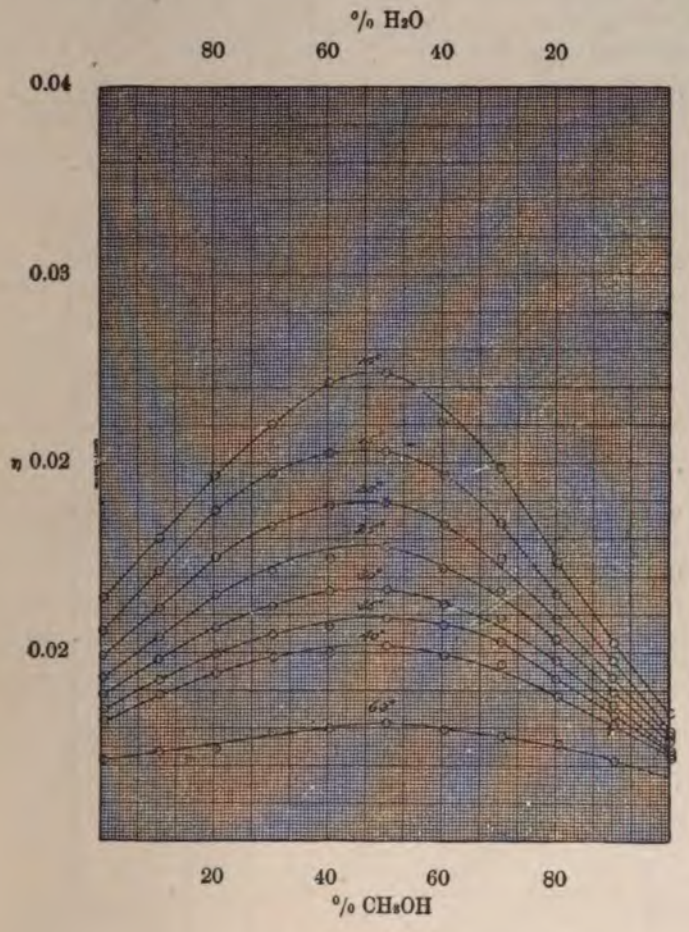

FIG. 16

series of temperatures. The absence of any points of discontinuity is immediately evident.

Kremann and Ehrlich also made viscosity measurements on mixtures of sulphuric acid and water at a series of temperatures. Their results are shown graphically in Figure 17. The curve for 0° shows a maximum (but not a point, as drawn in the figure) somewhere between

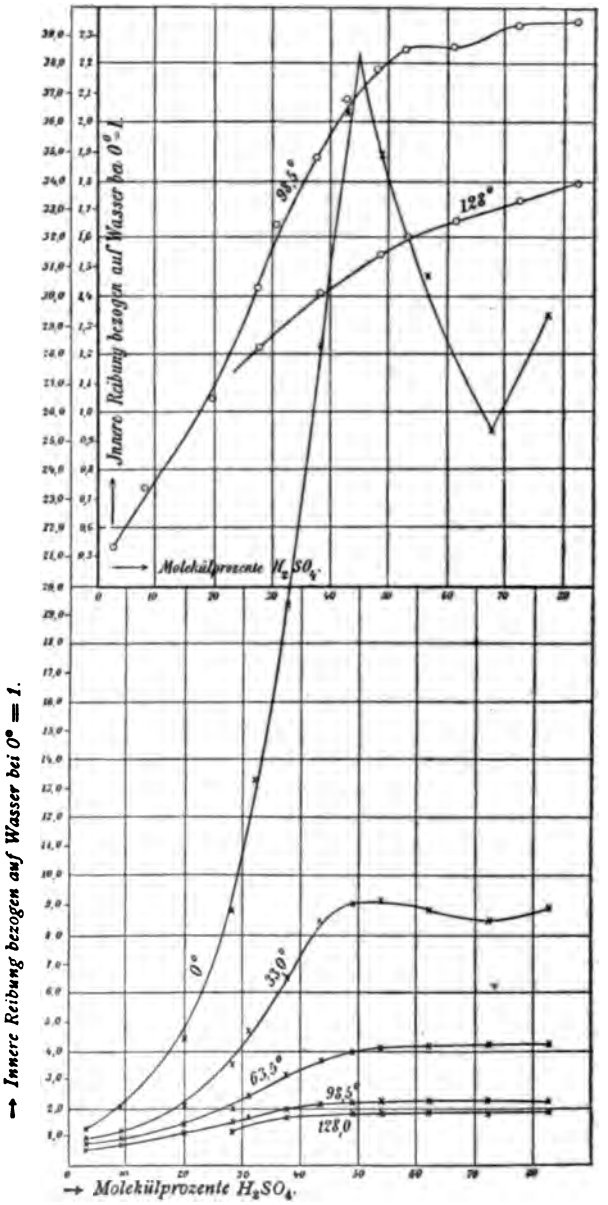
Innere Reibung bezogen auf Wasser bei 0° = 1.
Molekülprozente H_2SO_4.
98,5°
128°
0°
33,0°
63,5°
98,5°
128,0
Innere Reibung bezogen auf Wasser bei 0° = 1.
Molekülprozente H_2SO_4.

FIG. 17

40 and 50 mol per cent. and a minimum in the neighborhood of 70 mol per cent.[89] With rising temperature these irregularities become less and less marked, finally disappearing. The authors regard the position of the maximum as further evidence of the existence of the compound $H_2SO_4 \cdot H_2O$ in the solution.

Other Physical Properties. — The law of mixtures, applied to such properties as compressibility, surface tension, refractivity, magnetic rotation of the plane of polarization, etc., has been used but seldom in attacking the problem of complex formation in solution. The principles involved are quite similar to those discussed in the preceding sections, and it is not therefore necessary to treat them individually.[90]

Heat of Solution. — The law of mixtures requires that mixing of two normal liquids shall take place without absorption or evolution of heat. In cases where the process of solution consists to a large extent of a union between solvent and solute to form one or more hydrates in solution, a parallelism between heat of solution and degree of hydration in certain cases might be expected. Such a parallelism is found when the heats of solution of salts with a common anion are compared with other properties depending upon hydration, such as freezing-point and vapor-pressure lowering.[91] This parallelism is evident in the accompanying table[92] (Table XI), which contains the heats of solution (in joules) of a number of salts. Compare this review, page 364.

[89] Cf. Dunstan and Wilson, Trans. Chem. Soc., 91, 85 (1907).

[90] References: Veley and Manley, R. 75, p. 118. Röntgen and Schneider, Wied. Ann., 29, 196, 208 (1886). Whatmough, Z. physik. Chem., 39, 129 (1901). Knietsch, Ber. deutsch. Chem. Ges., 34, 4110 (1901). Linebarger, J. Amer. Chem. Soc., 22, 5 (1900). Ramsay and Ashton, J. Chem. Soc., 65, 167 (1899). Grünmach, Abhandl. Eich. Komm., 3, 174 (1902). Volkmann, Wied. Ann., 11, 194 (1880); 17, 368 (1882). Quincke, Pogg. Ann., 160, 347 (1877). Kremann and Ehrlich, Sitzungsber. Wien Akad., 116, 740 (1907). Bousfield, Phil. Trans., 206, 150 (1906). Getman and Wilson, Amer. Chem. J., 40, 468 (1908).

[91] As shown by Tammann, Mem. Acad. Sci., St. Petersburg (7), 35 (1887).

[92] From the paper of Biltz, R. 15, p. 211.

TABLE XI

HEATS OF SOLUTION IN JOULES

ALKALI GROUP

	NO_3.	SCN.	CN.	Cl.	Br.	I.
K	−36	−25	−12.6	−13	−21	−21
NH_4	−26	..	..	−17	−1	−15
Na	−21	..	..	−5	−1	+5
Li	+1	..	..	+35	..	..

ALKALINE EARTH GROUP

	Cl_2.	Br_2.
Ba	+9	+21
Sr	+46	+67
Ca	+73	+102
Mg	+100	..

The heat of solution of a solid salt is doubtless a composite quantity, including, as it does, the heats of disgregation, of ionization, etc., as well as heat of hydration, so that a parallelism is the most that could be expected. Heat of dilution of a concentrated solution would probably be a better basis for comparison if sufficient data were available.

The parallelism shown in Table XI between the heat of solution of the various salts and their effects upon the lowering of the freezing points is, nevertheless, very striking. In the case of the alkali salts, for example, the heat due to hydration apparently increases with decrease in atomic weight, becoming finally, in the case of lithium salts, sufficiently great to more than compensate for the negative heat of disgregation of the solid salt.

An extended discussion of the thermochemistry of aqueous solutions of electrolytes will be found in a paper by Bousfield and Lowry.[98]

Final Conclusions Regarding the Methods Depending upon Physical Properties. — In the general tendency of many investigators to attribute the peculiarities of the physical properties of concentrated aqueous solutions to the presence of hydrates, certain important relations brought

[98] "The Thermochemistry of Electrolytes in Relation to the Hydrate Theory of Ionization," Trans. Far. Soc., 3, 123 (1907).

out by Tammann[94] do not seem to have received the consideration which they deserve. Tammann has shown that, as regards many of its physical properties, a salt solution resembles the pure solvent under an increased external pressure Thus, for example, the phenomena which we have mentioned regarding the effects of salts upon the heat-capacity, viscosity, coefficient of expansion, etc., of the solvent can all be reproduced by simply subjecting the pure solvent to an increased external pressure.

There is considerable evidence to support the conclusion that water is a highly associated liquid, especially at low temperatures, and that the breaking down of the complex water molecules into simpler ones, such as occurs, for example, when the temperature is raised, is attended by a decrease in volume.[95] If this is the case, the effect of increasing the external pressure would be to cause a dissociation of complex molecules into simpler ones. The effect of pressure in decreasing the specific heat, specific volume, viscosity, etc, is more marked at lower temperatures, which is likewise the case for the effects of salts upon these properties.

These facts render it highly probable that a large part of the abnormal effects of salts upon the physical properties of water should also be ascribed to changes in the complexity of the solvent.[96] It may, indeed, be true that hydration is the mechanism by which these changes are brought about; but such a conclusion, drawn from the study of physical properties alone, must be regarded as highly speculative.

We are therefore forced to conclude, in spite of the extensive literature on this phase of the subject, that methods of studying hydration which depend upon the deviations of any physical property of a solution from the law of mixtures are incapable of yielding any *conclusive* information regarding the complexity or even the existence of hydrates in aqueous solution.

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[94] "Über die Beziehungen zwischen den inneren Kraften und Eigenschaften der Lösungen." Hamburg and Leipzig (1907).

[95] Sutherland has treated this subject extensively in a series of papers in the Philosophical Magazine, *q. v.* [6], 14, 1 (1907), and [5], 50, 460 (1900). See also Röntgen, Wied. Ann., 45, 91 (1891), and Stradling, J. Frank. Inst., 152, 257 (1901).

[96] This hypothesis, in various forms, has been advanced by numerous writers on the subject of aqueous solutions in recent years.

SECTION II. METHODS DEPENDING UPON DIFFUSION COEFFICIENTS AND IONIC MOBILITIES

Introduction

In this group are included those methods of studying hydration which depend upon kinetic or mechanical theories regarding certain properties of solutions and phenomena occurring in them. These methods have, up to the present time, been almost entirely confined to solutions of electrolytes, only a single instance of an application to a nonelectrolyte having come to my notice. This section of the review will therefore deal chiefly with that portion of the Ionic Theory which treats from a kinetic standpoint such phenomena as (1) ionic conductivities and diffusion coefficients, and the effects of changes of temperature, of concentration, and of the nature of the solvent upon these quantities; (2) the relation between the size of the ions and certain physical properties of the solution, such as density, viscosity, etc.; (3) transference effects accompanying electrolysis.

Owing to the nature of the methods included in this and the following section (which in some cases are based upon hypotheses which have not yet received general acceptance), I have endeavored, as far as practicable, to present the different theories in the words of the individual investigators.

The Hydration of Cane Sugar in Solution from the Standpoint of the Kinetic Theory

From purely kinetic considerations, Einstein[97] has recently derived the following expression connecting the viscosity coefficient, k, of a dilute solution with that, k_o, of the pure solvent, and with the volume, v, occupied by the solute molecules per unit volume of solution,

$$\frac{k}{k_o} = 1 + v.$$

In the derivation of this equation it is assumed that the solute molecules are spheres which are large in comparison with the molecules of the

[97] Einstein, "Eine neue Bestimmung der Molekül-Dimensionen," Ann. Phys. [4], 19, 301 (1906).

solvent among which they move. The author applied the formula to the data for a 1 per cent. sugar solution, and found that the presence of the sugar produced a greater effect upon the viscosity of the medium than was to be expected from the kinetic theory. He states his conclusions as follows (R. 97, p. 301): "Während also die Zuckerlösung, was ihre Dichte anbelangt, sich wie eine Mischung von Wasser und festem Zucker verhält, ist der Einfluss auf die innere Reibung viermal grösser, als er aus der Suspendierung der gleichen Zuckermenge resultieren würde. Es scheint mir dies Resultat im Sinne der Molekulartheorie kaum anders gedeutet werden zu können, als indem man annimmt, dass das in Lösung befindliche Zuckermolekül die Beweglichkeit des unmittelbar angrenzenden Wassers hemme, so das ein Quantum Wasser, dessen Volumen ungefähr das Dreifache des Volums des Zuckermoleküls ist, an das Zuckermolekül gekettet ist."

This conclusion is thus in qualitative agreement with the results of the methods discussed in Section I.

Comparative Ionic Hydration as Indicated by Ionic Conductances

The remarkable fact early attracted attention that, in the case of the ions of elements belonging to any one group of the periodic system, those of the elements of smaller atomic weights and smaller atomic volumes possess a lower equivalent conductance and therefore a smaller migration-velocity. A striking example of this is offered in the case of the alkali metals, as shown by the following table (Table XII), in which Column II contains the atomic weight of the element, Column III its atomic volume in the solid state, and Column IV the equivalent conductance of its ion at 18° as derived by Kohlrausch.

TABLE XII

I.	II.	III.	IV.	V.
	At. wt.	At. vol.	$l_{18°}$.	$k \cdot 10^7$.
Li	7.0	13.1	33.4	7.6
Na	23.0	23.7	43.5	7.4
K	39.1	45.5	64.6	6.0
Rb	85.5	56.0	67.5	5.3
Cs	132.9	7.1	68.0	5.2

This anomalous behavior is also shown by the viscosity coefficients of the ions, the ions of the larger and heavier atoms having the smallest viscosities.[98] As a possible explanation of this anomaly, Bredig[99] suggested that the lighter ion might have a larger cross-section or be so shaped as to offer a larger resistance. If such were the case, the rates of diffusion of these metals in mercury might be expected to show a similar behavior. This is not the case, however, as is shown by Column V of the above table, which contains the diffusion coefficients (k) of the alkali metals in mercury. The rates of diffusion are in the same order as would be expected from the atomic weights and atomic volumes of these elements.[100] To explain this apparent anomaly it has been assumed[98,99] that the ions are hydrated, those of the lighter elements in a given group being more hydrated (and therefore really larger and heavier) than those of the heavier elements. By referring again to Table XII and to page 364, Section I, of this review, it will be noticed that this assumption places the alkali elements in the same order as regards their relative degrees of hydration as was deduced from the relative effects of their salts upon the activity of the solvent. A direct proof of the correctness of this explanation, as well as a determination of the relative amounts of water in combination with some of these ions, has been described in a preceding communication (R. 120*a*).

Ionic Conductances as Affected by Changes in the Temperature and Viscosity of the Medium

More than a quarter of a century ago, and five years before the announcement of the Theory of Electrolytic Dissociation by Arrhenius, Stephan[101] studied the relation between the fluidity and the electrical conductivity of dilute solutions of electrolytes, and came to the conclusion that the ions were hydrated and carried a portion of the solvent with them as they moved through the solution; the evidence which led him to this conclusion being very similar to that which, twenty years later, caused Kohlrausch to propose a similar hypothesis as an

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[98] Euler, Wied. Ann., 63, 273 (1897).

[99] Bredig, Z. physik. Chem., 13, 277, N. 2 (1894).

[100] These diffusion coefficients are from an investigation by von Wogau, Ann. Phys., 23, 369 (1907). Euler has shown (R. 98) that a similar relation holds true for the diffusion coefficients of the halogens in non-aqueous solvents.

[101] Stephan, Wied. Ann., 17, 673 (1882).

explanation of the striking relationships between the values of the ionic conductances and their temperature coefficients. Stephan determined the fluidities and electrical conductivities of dilute solutions of the chlorides and iodides of the alkali metals in mixtures of alcohol and water of varying composition. He found that at constant temperature, but with varying amounts of alcohol, the conductances, Λ_∞, of very dilute solutions of these salts and the viscosities, η, of the medium obeyed the law,

$$\Lambda_\infty \eta = \text{const.}, \tag{34}$$

for mixtures all the way from pure water up to the mixture of maximum viscosity containing 50 per cent. of alcohol. This range includes a threefold increase in the viscosity, η, of the medium. As a further support of his conclusions he pointed out that the temperature coefficients of the conductances in the different mixtures and also in pure water were almost identical in every case with the temperature coefficients of the viscosity of the medium. These results pointed to the conclusion (R. 101, p. 700), "dass jedes Ionenmolecul die benachbarten Molecule des Lösungsmittels einfach mitnimmt."

Our knowledge regarding the conductivities and viscosities of solutions of electrolytes in mixed solvents has been greatly enlarged by the recent experiments of Jones and his co-workers.[102] Their experiments demonstrate clearly that in all cases a marked parallelism exists between the conductivity and the fluidity of the solvent. A minimum in conductivity is always accompanied by a minimum in fluidity, both occurring at approximately the same percentage composition. Further discussion of conductivity in mixed solvents would necessarily involve a consideration of the problem of solvation in general, which would lead us beyond the bounds of this review. The phenomenon of hydration in solution is only one part of the general problem of solvation in solution. It is not the purpose of the reviewer to discuss this problem in other solvents than water, however, and the reader interested in this phase of the subject should consult the excellent review by Carrara[103] of "The Electro-Chemistry of Non-aqueous Solutions."

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[102] Jones *et al.*, "Conductivity and Viscosity in Mixed Solvents," Carnegie Inst. Pub. No. 80 (1907). See also a recent investigation by Hartley, Thomas, and Applebey [Trans. Chem. Soc., 93, 538 (1908)]. These investigators studied solutions in mixtures of water and pyridine. They found that the $\Lambda_\infty \eta$ product decreased regularly with increase in pyridine content until the solvent contained 67 per cent. of pyridine. Compare also a recent paper by Pissarjewski and Karp [Z. physik. Chem., 63, 257 (1908)] on the relation between the diffusion coefficient, the viscosity, and the electrical conductivity of solutions.

[103] Carrara, Gaz. Chim. Ital., 37, I, 525 (1907); also Ahrens Sammlung, 12, 404 (1908).

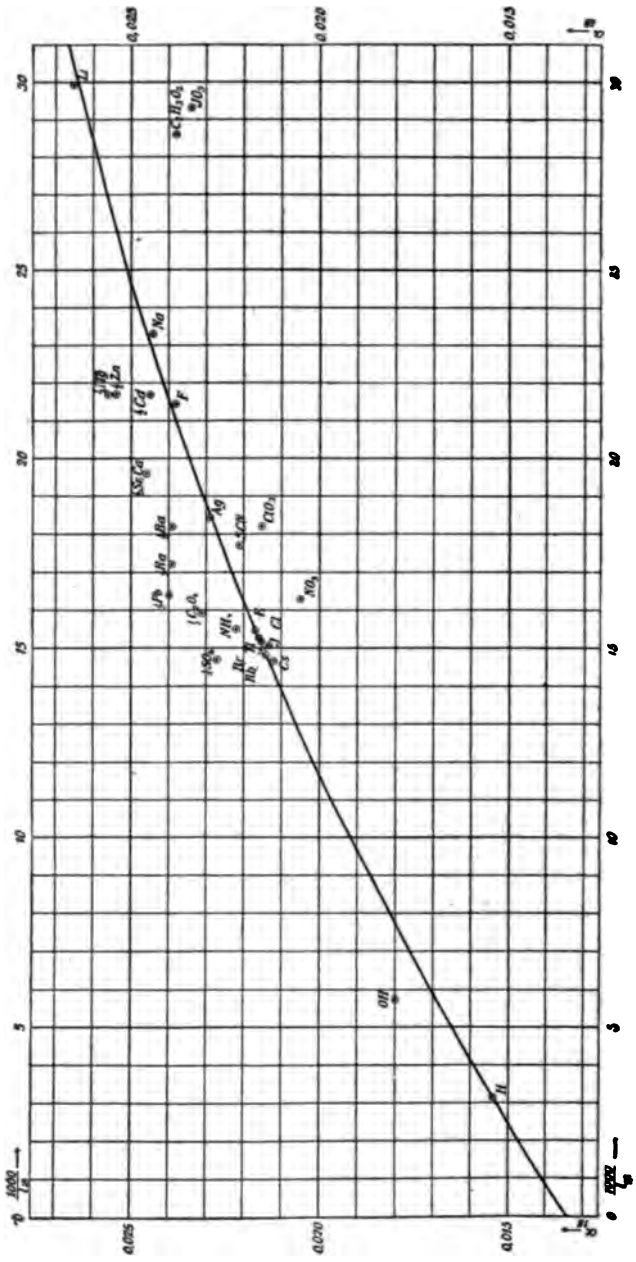

FIG. 18

The Hypothesis of Kohlrausch. — Fr. Kohlrausch has expressed the opinion [104] that the relationships existing between the values of the ionic conductances and their temperature coefficients are such that it is scarcely possible to understand them except on the hypothesis that "about every ion moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion," and that "the electrolytic resistance of an ion is a frictional resistance that increases with the dimensions of the atmosphere." One of the most important relationships which led Kohlrausch to this conclusion is the fact that the temperature coefficient, α, for the conductance, l, of a given ion is a function of the conductance itself, and can be expressed by the equation,

$$\alpha = a + b\left(\frac{1}{l_{18°}}\right) + c\left(\frac{1}{l_{18°}}\right)^2, \qquad (35)$$

where $a = 0.01341$, $b = 0.640$, and $c = 6.94$. The graph of this equation, together with the loci of the values of l for numerous ions, is shown in Figure 18.[105] The further presentation and discussion of the relations derived by Kohlrausch are presented in his own words (R. 105, p. 130): "Aus dem ganzen Temperaturverhalten muss man den Schluss ziehen, dass der Ionenwiderstand wesentlich bedingt ist durch Wasserhüllen, die dem Ion, je nach seiner Individualität in verschiedener Grösse, anhaften, d. h. mit ihm wandern. Dass ein, in einer Flüssigkeit enthaltenes Atom oder ein Atomkomplex daselbst nicht wandern kann, ohne Teile des Lösungsmittels mit zu ziehen, wenn das wandernde obendrein, so wie hier, elektrisch geladen ist, muss man von vornherein annehmen.

. . . "Macht man die Annahme, dass der elektrolytische Widerstand eines Ions wesentlich in dem molekularen Reibungswiderstand seiner Wasserhülle besteht, also um so grösser ist, je mehr Wasserteile mitwandern, so wird nun eine Reihe von Erscheinungen begreiflich, die sonst unvermittelt dastehen.

. . . "Die Temperatur wirkt auf den elektrolytischen Widerstand mit derselben Grössenordnung ein, wie auf die Viskosität des Wassers, und zwar nähern sich in dieser Hinsicht die wenigst beweglichen, *i. e.*, die durch eine dicke Wasserhülle ihrer Individualität am meisten entkleideten Ionen dem Temperaturkoeffizienten der Wasserreibung.

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[104] Kohlrausch, "The Resistance of the Ions and the Mechanical Friction of the Solvent," Proc. Roy. Soc., London, 71, 338 (1903).

[105] See Kohlrausch, Z. Electrochem., 14, 130 (1908).

"Weiter konvergieren die Formeln, welche die Temperaturabhängigkeit in weiteren Grenzen darstellen, nach unten verfolgt, nach ungefähr demselben Nullpunkt der Leitfähigkeit; zu nahe dem gleichen Nullpunkt für die Fluidität des Wassers führt auch die Temperaturformel der Wasserreibung."

The curves showing this extrapolation are given in Figure 19.[104] The fluidity of water when calculated in the same way as the conductivity, with the quadratic formula, is represented by the lowest curve. The extrapolated portions of all these curves pass through zero between $-35°$ and $-41°$.[106]

"Verstärkt werden diese Argumente dadurch, dass, wie ich vor 30 Jahren gezeigt habe, der elektrolytische Widerstand der Ionen, in mechanischen Einheiten gemessen, von derselben Grössenordnung ist, wie der mechanische Widerstand der Wassermoleküle, wenn man diesen aus der Reibungskonstante des Wassers und der, aus anderen Erscheinungen abgeleiteten Grösse der Moleküle berechnet.

"Endlich ist ja aber auch der Gegenstand dieses Aufsatzes, nämlich die Tatsache, dass die Beweglichkeit und ihr Temperaturkoeffizient bei so mannigfaltigen Körpern, wie Alkalimentalle, Fluor, Silber, Chlor, Thallium, durch ein und dasselbe Gesetz aneinander geknüpft sind, ohne eine Vermittelung fast widersinnig. Es muss offenbar etwas da sein, was die grundverschiedene Einzelnatur dieser Ionen aus dem Zusammenhange eliminiert hat. Dieses dritte, allen Vorgangen Gemeinsame kann man nur im Lösungsmittel suchen, und in der Tat, durch die Annahme, dass der Ionenwiderstand nicht die direkte Aeusserung einer Eigenschaft des Ions ist, sondern dass die direkte Wirkung des letzteren nur im Binden ungleicher Wasserhüllen besteht, wird der gesetzmässige Zusammenhang zwischen der Grösse der Beweglichkeit und der Grösse ihres Temperaturkoeffizienten, wenn auch vorerst noch nicht ins einzelne verfolgbar, doch wenigstens durchsichtig. Man ist nicht mehr verwundert, wenn der Temperatureinfluss auf Ionen von grossem Widerstand, d. h. von dicken Wasserhüllen, sich dem Einfluss auf die Reibung des Wassers selbst nähert. Dass der Temperatureinfluss auf die beweglicheren Ionen nicht genau derselbe ist, haben wir irgend einer Art von Mitwirkung des Ionenkernes zuzuschreiben, sei es einer direkten auf die Reibung im Lösungsmittel oder einer Wirkung,

[106] See also W. Hechler, "Fluidität und Leitfähigkeit einigen konzentrierter Salzlösungen unter 0°," Ann. Phys., [4], 15, 157 (1904); also R. Hosking, "Electrical Conductivity and Fluidity," Phil. Mag., [6], 7, 469 (1904).

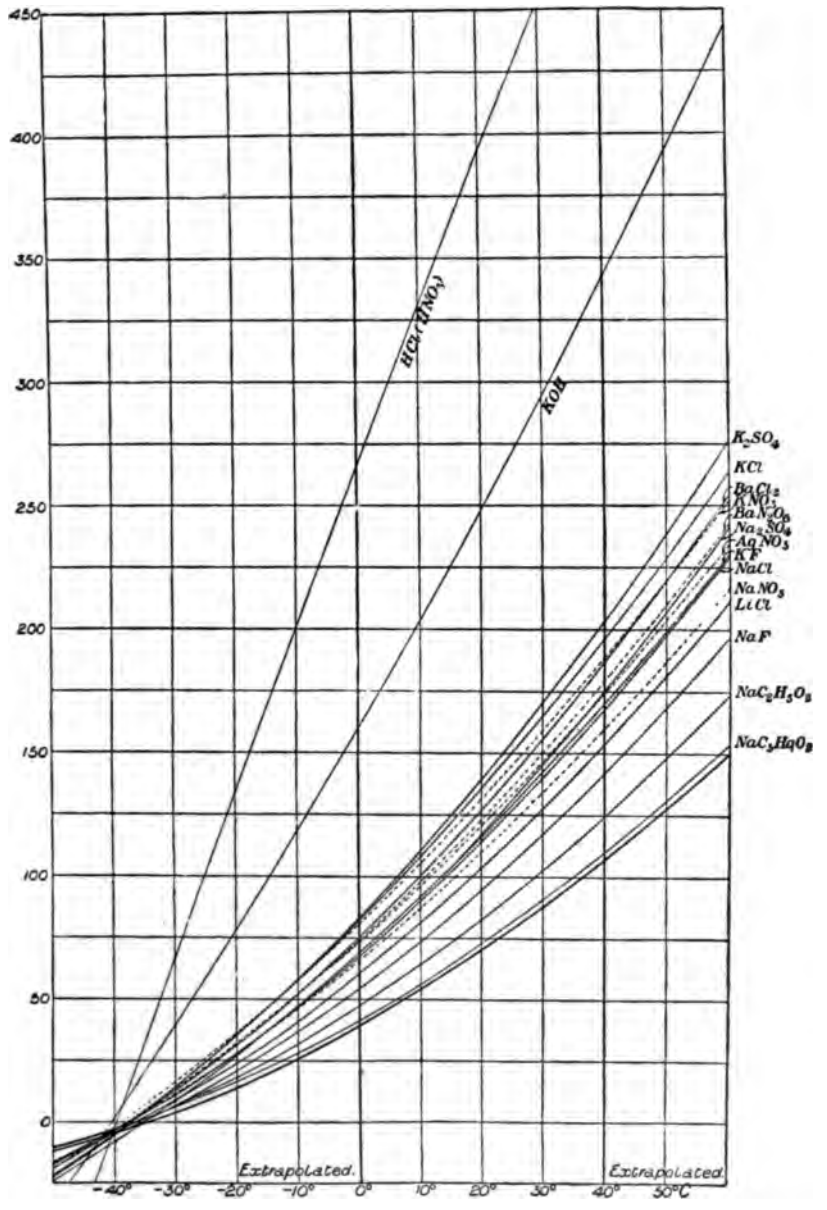
450
400
350
300
250
200
150
100
50
0
$Ba(NO_3)_2$
KOH
K_2SO_4
KCl
$BaCl_2$
KNO_3
BaN_2O_6
Na_2SO_4
$AgNO_3$
KF
NaCl
$NaNO_3$
LiCl
NaF
$NaC_2H_3O_2$
NaC_3Hq0_2
Extrapolated.
Extrapolated.
-40° -30° -20° -10° 0° 10° 20° 30° 40° 50°C

FIG. 19

die darin besteht, dass die gebundene Wassermenge von der Temperatur abhängt.

. . . "Ich halte die Hypothese, dass der Ionenwiderstand wesentlich durch die Menge mitgeführten Lösungsmittels bestimmt wird, jetzt schon für eine nicht zu bezweifelnde, und ich neige zu der Ansicht, dass die physikalische Chemie ernstlicher auf diese Vorstellung eingehen musste, als sie es bis jetzt tut."

Further relationships between the ionic conductances and the viscosity of the medium at different temperatures will be discussed in the next section.

The Size of Ions in Relation to the Physical Properties of Aqueous Solutions

In 1850 Sir George Stokes[107] considered the motion of a small sphere of radius, r, moving under a driving force, F, with a velocity, V, through a homogeneous viscous medium of viscosity, η, and deduced the following formula for its motion,

$$V = \frac{F}{6\pi\eta r} \tag{36}$$

This equation has received experimental confirmation in several cases, among which may be mentioned the experiments of H. S. Allen,[108] who has shown that the velocity of small bubbles of air rising through water or aniline agrees with that calculated by the above equation. Von Wogau[108a] has also recently applied the equation to the diffusion of metals in mercury.

Sutherland,[109] in 1902, attempted to apply Stokes's theory to the motion of the ions in solutions of electrolytes, under the assumption that they can be regarded as small spheres moving through a viscous medium, but abandoned the attempt because the theory required that the mobility of an ion should vary inversely with its radius, a condition which seemed to be contrary to the facts (the volume of the ion being assumed the same as that of the atom; see this review, page 415).

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[107] Stokes, Camb. Phil. Trans., 9, 58 (1850).

[108] Allen, Phil. Mag., [5], 50, 323 (1900).

[108a] R. 100; cf.. however, G. McP. Smith, Ann. Phys., 25, 252 (1908).

[109] Sutherland, Phil. Mag., [6], 3, 161 (1902).

This apparent discrepancy disappears (as we have seen, page 416) if the ion is surrounded by an atmosphere of the solvent, which moves with it through the solution. On this basis, therefore, the problem has recently been again attacked by W. R. Bousfield, who has considered the application of Stokes's theory to the motion of an ion, under the assumption that *the size of the ion is a function both of the temperature and of the concentration of the electrolyte.* The results of this consideration have recently appeared in two extensive papers [110, 111] by this author.[112]

It is by no means certain that it is justifiable to apply the Stokes's equation to the motion of an ion through a medium such as water, composed of particles whose dimensions are comparable with those of the ion itself. Nevertheless, Bousfield, starting with certain fundamental assumptions, has applied the Stokes equation to ionic mobilities, has developed numerous equations connecting the ionic volumes with various properties of the solution, and has found that the equations so derived are in agreement with the results of experiment. He reaches the conclusion that this agreement indicates the validity of his fundamental assumptions, the most important of which is the applicability of the Stokes equation. To the reviewer, however, it seems, as will be shown below, that these results tend, if anything, to disprove the assumption that the Stokes equation is applicable to ionic mobility. In the following treatment Bousfield's point of view and his results and conclusions are presented as completely as practicable within the limits of this review. In addition, the results and theories of other investigators of different phases of the subject are also presented, and the reviewer's interpretation is added in certain cases.

The Variation of the Size of Ions with the Temperature

If l_t and $l_{25°}$ represent the conductances of an ion (at infinite dilution) at $t°$ and 25°, respectively, it follows from Stokes's equation that

$$\frac{l_t}{l_{25°}} = \frac{r_{25°}\eta_{25°}}{r_t\eta_t} \quad \text{or} \quad \frac{r_t}{r_{25°}} = \frac{l_{25°}\eta_{25°}}{l_t\eta_t}. \tag{37}$$

[110] Bousfield, "Ionengrössen in Beziehung zur Leitfähigkeit von Electrolyten," Z. physik. Chem., 53, 257–313 (1905); and

[111] Bousfield, "Ionic Size in Relation to the Physical Properties of Aqueous Solutions," Phil. Trans. [A], 206, 101–59 (1906).

[112] See also papers by Carroll [Amer. Chem. J., 36, 594 (1906)]; Pellat [Compt. rend., 144, 902 (1907)]; and Carse and Laby [Proc. Camb. Phil. Soc., 14, 1 (1907)].

If Stokes's theory is applicable to the motion of the ion, the right-hand member of the latter equation represents the radius of the hypothetical ionic sphere in terms of its radius at 25° taken as unity. This quantity will be called the "radion" (25°), following the nomenclature used by Bousfield. If the only effect of temperature upon the conductance of an ion is that due to the change in the viscosity of the medium, the product, $l_t\eta_t$, should be a constant for all temperatures. If we compute values of the quantity, $\frac{l_t\eta_t}{\eta_{25°}}$, for a series of temperatures, we shall obtain an idea of the magnitude of the factors, other than viscosity, which determine the mobility of an ion in aqueous solution. This quantity is obviously the conductance of the ion at $t°$ compared with that at 25° and corrected for the change in the viscosity of the medium (on the assumption of proportionality), thus eliminating that factor. In terms of Stokes's theory, this quantity is inversely proportional to the "radion," and will therefore serve as a measure of the change in radius undergone by the hypothetical ionic sphere with change in temperature (compared with its radius at 25° as unity).[113] The figures for the different ions will also serve as a basis for comparison of their volumes with one another according to this theory.

[113] That portion of Bousfield's first paper which dealt with this subject (R. 110, p. 274) was withdrawn by him in his second paper (R. 111, p. 105, note) for the reason that the data used by him were largely based on determinations of the conductivities of 0.001 N solutions, and therefore included variations of the degree of ionization with the temperature. Moreover, they covered only a small temperature range (40°). Owing to the recent extensive investigations of A. A. Noyes and his co-workers [A. A. Noyes, "The Electrical Conductivity of Aqueous Solutions," Carnegie Inst. Pub. No. 63 (1907)], we are now, however, in possession of accurate data on the equivalent conductance at infinite dilution of a number of electrolytes at temperatures ranging from 0° to 306°. I have accordingly made use of these data in this section.

TABLE XV

VALUES OF $\frac{l_t \cdot \eta_t}{\eta_{25°}}$, SHOWING THE DEVIATION FROM PROPORTIONALITY BETWEEN CONDUCTIVITY AND FLUIDITY

Ion.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
K	80.8	76.4	74.8	71.0	68.0	65.8	63.6	62.2
Na	51.7	51.0	50.8	50.2	49.7	49.3	48.6	48.6
NH_4	81.5	77.0	75.4	71.5	68.4	66.2	63.8	62.6
Ag	64.8	63.4	62.8	61.3	60.4	59.8	58.7	58.3
½Ba	64.2	64.6	64.7	65.0	65.2	65.5	65.8	65.7
½Ca	61.0	61.3	61.4	61.7	61.8	62.0	61.9	62.2
⅓La	73.8	75.1	75.5	76.5	77.5	78.2	78.8	79.2
Cl	82.1	77.3	75.5	71.3	68.2	65.8	63.6	62.2
NO_3	80.8	73.0	70.8	64.4	60.1	56.9	53.7	51.7
Ac	40.7	41.0	41.0	41.2	41.2	41.3	41.2	41.3
½SO_4	80.6	80.0	79.7	79.3	78.5	78.2	77.5	77.4
½Ox	81.5	77.2	75.9	72.0	69.3	67.4	65.3	63.7
¼$Fe(CN)_6$	120.0	116.0	115.0	111.0	108.0	106.0	. .	. .
H	479.0	370.0	350.0	280.0	241.0	205.0	174.0	152.0
OH	209.0	202.0	192.0	175.0	157.0	140.0	126.0	115.0

Table XV contains the values[114] of this quantity for fifteen ions at eight different temperatures, ranging from 0° to 156°. For purposes of ready comparison, these data are plotted in Figure 20, temperatures being plotted as abscissæ and values of the quantity, $\frac{l_t \eta_t}{\eta_{25°}}$, as ordinates.

In terms of Stokes's theory the curves shown in this figure would indicate that the ionic volumes of Na, Ag, and Ac (acetate) are nearly constant throughout this range of temperature; those of Ca and Ba decrease slowly, and that of La more rapidly with rising temperature; and those of the remaining ions, including H and OH (shown in the table, but not in the figure on account of the size of the scale), increase

[114] This table and the accompanying figure were prepared in this laboratory by Dr. J. Johnston and are included in a publication by A. A. Noyes and J. Johnston [Carnegie Inst. Pub. (1909)], which will appear shortly. I am indebted to Prof. A. A. Noyes for permission to use them in this review. In the preparation of this table the transference number for potassium chloride was taken as 0.50 at all temperatures above 50°. The values for the viscosity of water were interpolated, graphically, from the data of Thorpe and Rodgers and of de Haas (Landolt and Börnstein).

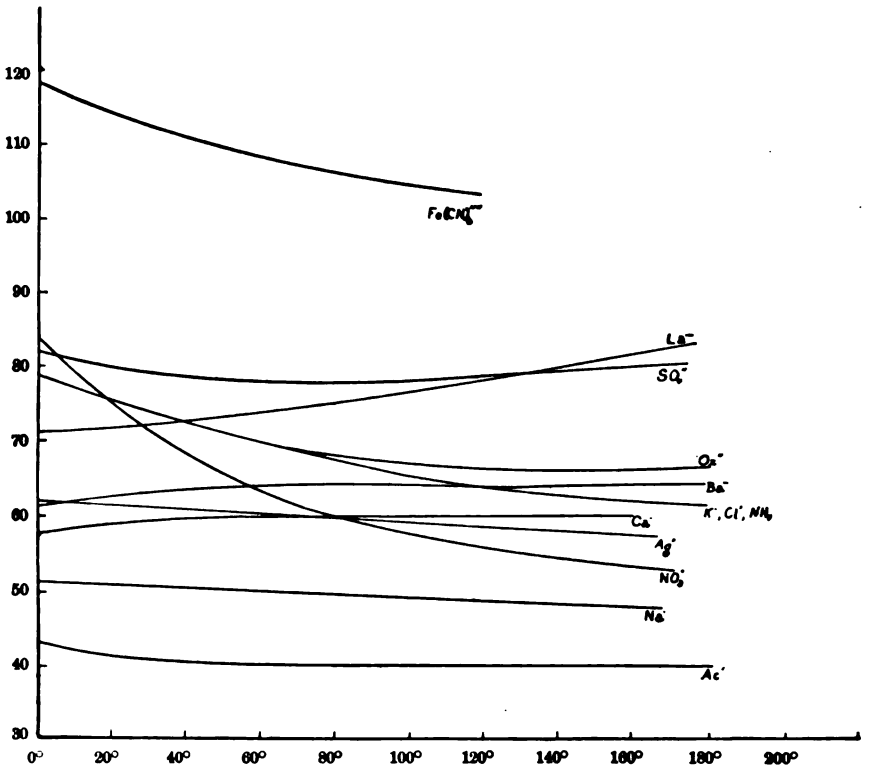

FIG. 20

with rising temperature. Bousfield seems inclined (R. 110, p. 277) to attribute these variations to corresponding changes in the degree of hydration. Such a conclusion requires that the degree of hydration of the majority of these ions increase, very rapidly in some instances, with rise in temperature, a conclusion which is at variance with most of the evidence regarding the sign of the heat of hydration.

The Variation of Ionic Size with Concentration. — According to Bousfield (R. 110, p. 273) the volume of an ion varies with the concentration of the electrolyte in a manner that may be expressed by the equation,

$$\frac{r_\infty}{r} = 1 + \varphi(h), \tag{38}$$

r_∞ and r being the radii of the hypothetical ionic spheres at infinite dilution and at the dilution h, respectively. $\varphi(h)$ denotes some function of the dilution h, the latter quantity being expressed as mols of water

per mol of solute. By combining this equation with Stokes's equation (36), it is shown to follow directly that the degree of ionization, γ (in solutions so dilute that the dielectric constant of the medium can be assumed to be the same as that of pure water), is expressed by the equation,

$$\gamma = \frac{\Lambda}{\Lambda_\infty} \cdot \frac{1}{F} \cdot \frac{1}{1 + f(h)}, \tag{39}$$

where F is the fluidity of the solution referred to that of water, at the same temperature, as unity.

The "true" value of γ, as given by this equation, cannot be calculated until the value of the unknown $f(h)$ is determined. To evaluate this function, the author assumes that the "true" value of γ is such that if it be substituted in the van't Hoff dilution law, *i. e.*,

$$\frac{\left(\frac{\gamma}{h}\right)^3}{\left(\frac{1-\gamma}{h}\right)^2} = K, \tag{40}$$

this law will hold exactly. Using Kohlrausch's values for the conductances of KCl solutions at 18°, the author combines equations (39) and (40) and evaluates $f(h)$ for this salt by a series of approximations, finally obtaining the result,

$$f(h) = 3.33h^{\frac{1}{2}}.$$

Values of γ for KCl solutions at 18°, calculated by the relation,

$$\gamma = \frac{\Lambda}{\Lambda_\infty} \cdot \frac{1}{F} \cdot \frac{1}{1 + 3.33h^{\frac{1}{2}}}, \tag{41}$$

are found by the author to satisfy the van't Hoff dilution law with a maximum error of 1 part in 2,000 up to a concentration of 0.2 molal. According to these results, equation (38) takes the form,

$$\frac{r_\infty}{r} = 1 + Bh^{\frac{1}{2}}, \tag{42}$$

where B is a constant characteristic of the ion in question. The author evaluates B for sodium, potassium, and chloride ions by means of a relation between this value and the transference number, which will be referred to later (page 434). With the equations so obtained, he computes a set of values showing the change of r^3 with the concentration. These values are given in Table XVI below, together with their sum

for each salt, this latter quantity being called the "ionic volume" of the salt in question and being denoted by the symbol I_v.

TABLE XVI

Salt.	P.	$r_K^3 \times 10^6$.	$r_{Cl}^3 \times 10^6$.	I_v
KCl	0	3.692	3.569	7.261
	1	3.128	2.968	6.096
	3	2.627	2.448	5.075
	6	2.163	1.981	4.144
	Normal	2.029	1.852	3.881
NaCl	0	12.107	3.569	15.676
	1	10.848	2.876	13.724
	3	9.648	2.303	11.951
	Normal	8.578	1.862	10.430

It will be noticed that all of the foregoing deductions are based upon the two assumptions, (1) that the Stokes equation can be applied to the motion of the ion, and (2) that the van't Hoff dilution law is a true and accurate expression for the change of the ionization with the dilution; neither of which assumptions seems very plausible, although they have led the author to several very interesting empirical relationships, as we shall see in the following sections. A strong argument against the validity of these hypotheses is to be found in the results shown in the above table. On examining the values of r^3 for each ion, we notice at once that the volume of the ion, and therefore the size of the water atmosphere and consequently the degree of hydration in each case, increases rapidly with the dilution, as the Mass-Action Law requires that it should. But the Mass-Action Law also requires that the degree of hydration shall reach a constant value in dilute solution as soon as the activity (active-mass) of the water becomes constant. Now in a 1 per cent. solution of potassium chloride the activity of the water, as measured by its vapor pressure, has become practically constant, differing only about 0.4 per cent. from its value at infinite dilution. Consequently no great change in the degree of hydration can take place between this concentration and infinite dilution. The above table, however, shows a change of about *20 per cent.* in the volumes of the potassium and chloride ions over this range of concentration.

The Size of Ions in Relation to Density

Bousfield compares the "solution volume, V_s" (*i. e.*, the apparent molecular volume of the solute in solution calculated on the assumption that the volume of the water in the solution is the same as in the pure state), with the "ionic volume, I_v," on the assumption that (R. 111, p. 126) "the solution volume derived from density observations is a measure of the amount of contraction which takes place on solution, and therefore a measure of the amount of water entering into combination with the solute. The ionic volumes at different dilutions should be nearly proportional to the amounts of water in combination with the ions, if the volume of water is large compared with the volume of the ionic nucleus. Hence, if our theory is correct, we ought to find the solution volume approximately a linear function of the ionic volume of the pairs of ions in dilute solutions."

On comparison of these quantities for solutions of KCl and NaCl from 0 to 6 per cent. concentration, the relation between the two quantities is found to be a linear one. From this relation the author deduces a "rational-density formula," by means of which the density of a solution is expressed as a function of the quantity, I_v, the latter quantity being determined from conductivity measurements in the manner indicated. The densities of NaCl and KCl solutions calculated by this formula are shown to agree with the observed values within the experimental error (fifth decimal place) up to molal concentration.

The Size of Ions in Relation to Viscosity

We have already (this review, Sec. I, p. 408) discussed the viscosity of solutions in its relation to hydration from the standpoint of the law of mixtures. There remains only to mention briefly some of the theories and hypotheses which have been advanced with the idea of "explaining" the viscosity of solutions of electrolytes by variations in the size of the individual molecules of the components.

We have mentioned elsewhere the fact that the viscosities of the different ions exhibit the same anomaly as do their migration velocities. Euler[115] has, in fact, shown that the relation between the viscosity constant, k, of an ion and its equivalent conductance, l, can be expressed by the simple equation,

$$(k - 0.68)l = \text{const.} \qquad (43)$$

[115] Euler, Z. physik. Chem., 25, 539 (1898).

The ions, NH_4, K, Rb, Cs, Tl, and NO_3, in aqueous solution tend to lessen the viscosity of the medium, so that solutions of many of their salts exhibit a lower viscosity than pure water. The electro-striction hypothesis, as proposed by Nernst and Drude [116] to explain this phenomenon of "negative viscosity," seems to be no longer sufficient to explain all the facts, since it has been shown by Wagner [117] and Mullenbein [118] that the same phenomenon occurs in non-conducting mixtures of organic liquids.

Most of the recent investigators [119] in this field have advanced some form of a hydrate hypothesis to explain the phenomenon, and such a hypothesis seems to accord well with the facts. This hypothesis is stated by Blanchard [120] as follows: "If now ions exist as hydrates, instead of simply as electrically charged atoms or radicals, they must be built up at the expense of the polymerized water molecules. Now it would seem highly probable that some of the hydrated ions, $M \cdot nH_2O$, might have a smaller mass, or, at least, a more symmetrical structure, than the $(H_2O)_x$ molecules of pure water. In such a case there might well be less friction to their motion than to that of the molecules of pure water. It is important to note that complexes between undissociated molecules of solute and molecules of solvent may be formed as well as the solvates of ions. With decreasing temperature the polymerization of water increases The formation, at least, of some of the possible polymers is attended by an expansion (which between 4° and 0° C. exceeds the normal contraction). Pressure thus will lessen the amount of polymerization and also lessen the viscosity, since polymerization obviously causes increased viscosity. At 32° C. the critical point is reached, where the polymerization of water is so slight that it is not decreased by pressure. The formation of solvates takes place to a lesser extent the higher the temperature. At higher temperatures there are also fewer molecules of polymerized water whose concentration will be diminished by the formation of hydrates. At 32° the effect of certain salts in lessening the viscosity, as well as that of pressure, becomes zero."

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[116] Nernst and Drude, Z. physik. Chem., **15**, 79 (1894).

[117] Wagner, Z. physik. Chem., **46**, 872 (1903).

[118] Mullenbein, Diss. Leipzig (1901).

[119] See, however, Jones, Carnegie Inst. Pub. No. **80**, 213 (1907); and Getman, J. Chim. Phys., **5**, 544 (1907); also Wagner (R. 117).

[120] Blanchard, "The Viscosity of Solutions in Relation to the Constitution of the Dissolved Substance," J. Amer. Chem. Soc., **26**, 1318 (1904).

Blanchard also adduces further evidence in support of this hypothesis. He finds (R. 120, p. 1330) that "addition of 2 and 4 mols, respectively, of ammonia to solutions of silver, copper, and zinc salts decreases very greatly the viscosity. Probably the degree of ionization of the metal-ammonia salts is slightly greater than that of the plain metal salts. This will, however, hardly account for the large decrease in viscosity, for Wagner [117] found, without taking ionization into account, that the viscosity of salts is, in general, very nearly equal to the sum of definite values assigned to each of the metallic and acidic atoms or radicals, respectively. . . . The only way, then, open to account for the decreased viscosity seems to be a decrease in size or an increase in symmetry of the salt molecules, or more especially of the positive ions of the salts (since ammonia is shown by migration experiments to form a part of that ion). If the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules cannot decrease its mass, and it is not easy to imagine that it can increase its symmetry. The only explanation, then, seems to be that metal ions in solution are hydrated; the hydrate-water is replaced by ammonia, which forms, with the ion, a more stable complex and one of less mass or greater symmetry, or both. It will be seen that this explanation of the lowering of viscosity of a metal salt solution by addition of ammonia is similar to the one offered earlier in this paper of negative viscosity."

Bousfield holds similar views. He remarks (R. 111, p. 129) "that it seems, *a priori*, probable that the *change of viscosity* caused by the introduction of foreign molecules into water would depend upon the number and size of the molecules so introduced. According to the theory postulated, an ion is a compound molecule, consisting of the ionic nucleus with its envelope of water molecules, as are also the un-ionized molecules of the solute. Hence, if the theory be true, we should expect to find a close relation between the viscosity of the solution and the number and size of these aggregates. The number of molecules depends upon the concentration, n, and the *size* upon the 'radions'; the product, $n(r_1 + r_2)$, should therefore be a measure of the joint effect of the introduced ions upon the viscosity in dilute solutions." In Table XVII are set out the concentrations and the observed and calculated viscosities for KCl and NaCl solutions. The "calculated" viscosities are computed from the formula,

$$\eta = a - bn(r_1 + r_2), \tag{44}$$

a and b being constants peculiar to the salt in question. The viscosity is thus seen to be a linear function of the quantity, $n(r_1 + r_2)$. The investigator also finds that a combination of the two viscosity equations for NaCl and KCl solutions yields an equation which expresses accurately the viscosity of various mixtures of these solutions. The author then proceeds to develop a general viscosity formula based upon his hypothesis. To follow this discussion further would lead too far from the subject of the present review, and the reader who is interested in further details should consult the original (R. III, pp. 134–142).

TABLE XVII

n.	η.	η.
	Observed.	Calculated.
0.0	0.010514	0.010514
0.1347	0.010504	0.010491
0.2712	0.010465	0.010470
0.4094	0.010445	0.010450
0.5493	0.010419	0.010430
0.8344	0.010393	0.010391
1.000	0.010374	0.010374

In speaking of the agreement between observed and calculated values in Table XVII, Bousfield remarks: "The agreement between observed and calculated values is sufficient to show that the *chief element* which determines the viscosity of the solutions is the product, $n(r_1 + r_2)$. . . . The results tend strongly to confirm the fundamental hypothesis as to the character of the magnitudes which we have called 'radions,' and which we derived from the conductivities by the application of the Stokes theorem and the van't Hoff law."

Is this conclusion justified? Bousfield's investigations have yielded some very valuable data on the viscosities and densities of aqueous salt solutions, and from his fundamental hypotheses he has derived formulæ for the density, the viscosity, and the conductivity of a salt solution and of a mixture of two salt solutions (R. III, p. 125). He has tested these formulæ by means of experimental data on KCl and NaCl solutions, and found that they express the facts accurately, in some cases (notably the density formulæ) even more accurately than any empirical formula previously proposed. Nevertheless, it is to be remembered that the funda-

mental hypotheses of this investigator — namely, the validity of Stokes's equation for ionic mobilities and the validity of the van't Hoff Dilution Law as applied by him — must be regarded as purely arbitrary hypotheses, of little *a priori* probability, and with the weight of evidence against them, as shown by some of the conclusions to which they have led the author (see pages 426, 428, and 434 of this review). What, then, is the explanation of the excellent agreement between the observed results and those calculated by the author's formulæ?

The reviewer is of the opinion that the probable explanation is that, although these formulæ are seemingly theoretical ones, they are, in reality, simply empirical expressions connecting the concentration and the property in question, the excellent agreement being produced by the number of arbitrary constants to be evaluated from experimental data. To illustrate, consider the viscosity formula, equation (44). This equation contains two constants (a and b) to be evaluated by experiment. If we substitute for r_1 and r_2 the expressions by which they are computed (R. III, p. 125), we obtain

$$\eta = a - bn\left(\frac{1}{l_1(1 + B_1 h^{-\frac{3}{2}})} + \frac{1}{l_2(1 + B_2 h^{-\frac{3}{2}})}\right). \qquad (45)$$

This is an equation connecting, in a rather complicated manner, the viscosity, η, and the concentration, n, of a solution with the equivalent conductances of its ions, l_1 and l_2, and containing at least two constants to be determined by experiment. It is such an equation as would be obtained by combining two functions of the forms,

$$f(n, \eta) = 0 \text{ and } f(n, l) = 0, \qquad (46)$$

for each ion, and its agreement with the results of experiment is not, therefore, to be regarded as evidence either for or against the author's fundamental assumptions. Indeed the term, $Bh^{-\frac{3}{2}}$, in the above equation, which is the only portion of it which has any connection, even remotely, with Stokes's theorem and the van't Hoff dilution law as applied by the author, might be omitted entirely without seriously impairing the value of the equation as an accurate empirical relation.

Additional Relations

In addition to the relations which we have discussed, Bousfield finds, as one of the deductions from his hypotheses, that the Hittorf transfer-

ence number should be a linear function of the ratio of the radions. Using the ordinary values of transference numbers for KCl and NaCl, he finds that this conclusion agrees with the facts. This result is, however, if anything, an argument against his hypotheses, for, as we have seen (R. 120*a*), the Hittorf transference numbers which he used are not real transference numbers at all, since their calculation is based upon an erroneous assumption.

Neither, in the reviewer's opinion, can any importance be attached to the relation deduced by the author, that "the freezing-point depression is a linear function of the 'ionic volume,'" for further details of which reference must be had to the original (R. 111, p. 142).

The Determination of the Hydration of Ions by Transference Experiments

The description of this important method, together with the results obtained by it, has been given in a preceding communication,[120a] and will therefore not be discussed in this review.

SECTION III. MISCELLANEOUS METHODS

Hydration in Solution from the Standpoint of the Theories of the Constitution of Inorganic Compounds

A review of the subject of hydrates in solution which did not include a chapter dealing with the subject from the standpoint of the theory of Werner and that of Abegg and Bodländer would be incomplete. The subject of hydration in aqueous solution constitutes, however, only a small, if important, part of either of these theories, so that in the present review it will be necessary to assume, on the part of the reader, a familiarity with the general outlines of the two theories. The following presentation will, so far as practicable, be given in the author's own words.

The Theory of Werner.[121, 122, 123] — In 1893 Werner expressed the

[120a] This QUARTERLY, 21, No. 3, 287 (1908).

[121] Werner, "Beitrag zur Konstitution anorganischer Verbindungen. 'V' Über den Zustand der Metallsalze in wässeriger Lösung," Z. anorg. Chem., 3, 294 (1893).

[122] Werner, "Neuere Anschauungen auf dem Gebeit der anorganischen Chemie," Braunschweig (1905).

[123] Werner, "Zur Theorie der Basen," Ber. Chem. Ges., 40, 4133 (1907).

opinion that combination with the solvent was a necessary precedent to electrolytic dissociation. This view seems to have been derived by this eminent investigator solely as a deduction from his general theory regarding the constitution of inorganic compounds, since at the time of its publication there was little evidence indicating that ions are hydrated, an ion being almost universally regarded simply as an atom or radical possessing an electric charge and maintaining an independent existence within the solution. Werner was therefore one of the first to suggest a hydrate theory of ionization.[124] His views are therefore particularly interesting at the present time.

According to Werner (R. 121, p. 294): "Wir haben, wie es schon früher formuliert wurde, die wasserhaltigen Salze nicht als MX + aq zu schreiben, sondern (Maq)X; also wasserhaltiges Chlorcalcium nicht $CaCl_2$ + 6 aq, sondern $Ca(H_2O)_6Cl_2$. Negative Radikale, welche sich in direkter Bindung mit dem Metallatom befinden, sind keine Jonen; damit ein negativer Rest als Jon wirken könne, ist als erste Bedingung die Bildung des Hydrates, also Bildung der Salze wasserhaltiger Metallradikale, erforderlich. . . .

"Nach der Anschauung, wie sie sich aus unseren Betrachtungen ergiebt, ist die Existenz von Hydraten in wässeriger Lösung nicht nur im Sinne der Hydrattheorie anzunehmen, sondern diese Hydrate bilden auch die erste unumgängliche Bedingung zur elektrolytischen Dissoziation. Wir haben in wässeriger Lösung als Jonen nicht Metallatome, sondern Metallatome umgeben mit sechs an sie geketteten Wassermolekülen, mit denen sie geradezu zusammengesetzte Radikale bilden. Damit wird nun auch klar, warum das elektrolytische Leitvermögen, die Dissoziation der Salze in so grosser Abhängigkeit steht vom Lösungsmittel. *Nur solche Lösungsmittel sind befähigt, elektrolytische Dissoziation zu bedingen, welche mit den Metallsalzen zu analogen Radikalen zusammentreten können,* so in beschränktem Masse Alkohole, wie aus der Existenz von Verbindungen wie $Ca(C_2H_5.OH)_6Cl_2$; $Ca(C_2H_5.OH)_6(NO_3)_2$ hervorgeht.

"Die nächste wichtige Frage, die sich aufwirft ist die nach der *Natur der Hydratbildung.* Dieselbe wird in präciser Form durch unsere Entwicklungen beantwortet. In jedem wasserfreien Salze haben wir direkte Bindung zwischen Metall und Säurerest anzunehmen. Das Wasser besitzt nun die Eigenschaft, je nach dem Metall mit grösserer oder geringerer Leichtigkeit sich zwischen Metallatom und Säurerest

[124] Cf. Ciamician, Z. physik. Chem., 6, 405 (1890).

einzuschieben und so aus der direkten Bindung eine durch das Wassermolekül vermittelte indirekte Bindung zu schaffen.

"Die dadurch entstehenden Radikale, bestehend aus Metall und Wasser, können aber die verschiedensten Grade der Beständigkeit zeigen. Sie können in ihrer höchsten Form $M(H_2O)_6$ beständig sein, . . . , sie können aber auch, . . . in festem Zustande mit weniger Wasser auftreten. In wässeriger Lösung, wenigstens in verdünnter, werden sie wohl alle der Form $M(H_2O)_6$ entsprechen, und dies wird bedingt werden durch die Massenwirkung des Wassers.

"Diese Hydrate können aber auch in manchen Fällen nur in Gegenwart von viel Wasser als solche bestehen, was z. B. in den Kaliumsalzen der Fall zu sein scheint. Dieselben Krystallisieren meistens wasserfrei, leiten aber dennoch in wässeriger Lösung ausgezeichnet." . . .

"Zum Schlusse dieser Betrachtung wiederholen wir:

"*Die erste Bedingung zur elektrolytischen Dissoziation eines Salzes ist die Fähigkeit seines Metallatoms, sich mit einer bestimmten Anzahl von Wassermolekülen zu einem Radikal zu verbinden, in dem wir uns die Wassermoleküle so angeordnet zu denken haben, dass eine direkte Bindung zwischen dem Metallatom und dem Säurerest nicht mehr eintreten kann.*"

Werner's views regarding the mechanism of the process of ionization as a phenomenon of hydration are expressed as follows (R. 121, p. 323): "Denken wir uns das Metallatom als Kugel, die sechs mit demselben direkt verbundenen Komplexe in einer ersten um dasselbe beschriebenen Sphäre sich befindend, und die anderen ausserhalb dieser ersten Sphäre sich befindenden Reste als in einer zweiten Sphäre liegend, so können wir für sämtliche betrachtete Verbindungen den allgemeinen Satz aufstellen: Die Valenz des durch das Metallatom und die sechs mit ihm verbundenen Komplexe der ersten Sphäre gebildeten Radikals (MA_6) ist gleich der Differenz der Valenz des Metallatoms und der Valenz der einwertigen Gruppen der ersten Sphäre, ganz unabhängig von der in der ersten Sphäre vorhandenen Moleküle wie H_2O, NH_3 u. s. w.

"Dies wird sofort an folgenden Beispielen klar werden:

$$(Co(NH_3)_6)\ 3 - 0 = 3 :\ (Co(NH_3)_6)X_3$$

$$\left(Co^{(NH_3)_3}_{(NO_2)_3}\right)\ 3 - 3 = 0 :\ \left(Co^{(NH_3)_3}_{(NO_2)_3}\right)$$

$$\left(Co^{(NH_3)_2}_{(NO_2)_4}\right)\ 4 - 3 = 1 :\ \left(Co^{(NH_3)_2}_{(NO_2)_4}\right)K$$

u. s. w.; dieser Satz besitzt allgemeine Gültigkeit.

"Es besteht also ein charakteristischer Unterschied in der Wirkungsweise von Wasser- und Ammoniakmolekülen und derjenigen einwertiger Radikale. . . .

"Die Wirkungsweise der Moleküle wie NH_3, H_2O u. s. w. ist eine spezifisch ganz eigenartige; sie kann etwa folgendermassen definiert werden: Diesen Molekülen kommt die Eigenschaft zu, die Wirkungstellen der Affinitätskraft des Metallatoms aus der ersten Sphäre, in der sie im allgemeinen zur Thätigkeit gelangt, in eine vom Metallatom weiter entfernte Sphäre zu verlegen.

"Um dies durch eine Vorstellung, welche aber keine Beziehung zwischen den beiden Phänomenen andeuten soll, zu versinnlichen, sei diese Wirkungsweise folgendermassen mit einem elektrischen Phänomen verglichen. Denken wir uns das Metallatom als Kugel, geladen mit positiver Elektrizität, und die Wassermoleküle als neutraler Mantel um dieselbe gehüllt, so wird sich in diesem neutralen Mantel negative Elektrizität auf der inneren Mantelfläche ansammeln, wahrend auf der äusseren sich positive ansammeln wird. Die äussere Mantelfläche wird also nach dem ausserhalb gelegenen Raume nämliche Mengen positiver Elektrizität zur Wirkung bringen können, wie vorher das Metallatom. War der Mantel nicht vollständig neutral, sondern z. B schwach positiv, so wird dadurch die nach der zweiten Sphäre hin zur Wirkung kommende positive Elektrizitätsmenge um den gleichen Betrag verstärkt erscheinen.

"Ganz in derselben Weise erscheint nun die Wirkungsweise der Wasser-und Ammoniakmoleküle. Sie übertragen die Affinität nach einer weiter ab vom Metallatom liegenden Sphäre, und das Ammoniak, welches anscheinend einen etwas positiven Komplex darstellt, besitzt die Eigenschaft, gleichzeitig mit dieser Übertragung den positiven Charakter der Affinitätswirkung zu verschärfen. Wir haben früher aus der Betrachtung der Metallsalze in Lösung den Schluss gezogen, die erste Bedingung zur elektrolytischen dissoziation eines Salzes sei die Fähigkeit seines Metallatoms sich mit einer bestimmten Anzahl von Wassermolekülen zu einem Radikal zu verbinden. Wir haben uns nun eine Vorstellung gebildet über die Rolle dieser Wassermoleküle. Denken wir uns nun das Salz eines solchen Hydrats $M(H_2O)_6$, z. B. $M(H_2O)_6X_3$ in Wasser gelöst. Da dem Wasser schon die Fähigkeit zukam, die Wirkung der Affinitätskraft aus der ersten Sphäre in eine zweite zu verlegen, so ist nichts natürlicher als anzunehmen, dass die Wassermoleküle, von denen das Hydratsalz $M(H_2O)_6X_3$ in seiner Lösung in

Wasser umgeben ist, auch wieder die Eigenschaft besitzen werden, die Wirkung der Affinitätskraft, welche im Hydrat zunächst in einer zweiten Sphäre zur Thätigkeit gelangt, auch noch auf eine weitere Entfernung zu übertragen, indem sie um den ersten neutralen Mantel einen, allerdings nur in Gegenwart von überschüssigem Wasser beständigen zweiten neutralen Mantel bilden werden, um diesen zweiten einen dritten u. s. w. Die Folge davon wird eine vollständige Trennung des positiven und negativen Komplexes des Salzes sein, wir gelangen auf diesem Wege zur elektrolytischen Dissoziation der Salze in wässeriger Lösung und gleichzeitig zur Vorstellung, dass diese Dissoziation durch die Eigenschaft des Wassers, als Kraftüberträger zu wirken, bedingt wird." See also a more recent paper (R. 123, p. 4133).

An interesting application of Werner's theory is the explanation of the peculiar behavior, in solution, of the green and violet hydrates of chromium chloride. These unique compounds seem to belong to a class of hydrates of which few examples are known. The grayish blue hydrate, $CrCl_3 \cdot 6H_2O$, gives a violet solution in water. All three chlorine atoms are ionized in this solution, as shown by conductivity and cryoscopic measurements and by the fact that the chlorine is completely precipitated by silver nitrate. This hydrate corresponds to the hexammonia complex, $[Cr(NH_3)_6]Cl_3$, and its formula should therefore be written, $[Cr(H_2O)_6]Cl_3$, according to Werner's theory. The green hexahydrate gives a green aqueous solution, in which only one of the chlorine atoms is ionized, and consequently only part of the chlorine is precipitated in the cold by silver nitrate. In terms of Werner's theory, these relations are expressed by the formula,

$$[Cr^{Cl_2}_{(OH_2)_4} + 2H_2O]Cl.$$

On standing, the green solution changes slowly into the violet one, the reaction being

$$[Cr^{Cl_2}_{(OH_2)_4}]^+ + 2H_2O = [Cr(H_2O)_6]^{+++} + 2Cl^-.$$

This reaction seems to resemble that of the hydration of milk sugar in that it is a slow hydration in solution accompanied by an intramolecular rearrangement (cf. this review, Sec. I, p. 394). In addition to these two forms the theory provides for the existence of the forms,

$$[Cr^{Cl_3}_{(OH_2)_3} + 3H_2O] \quad \text{and} \quad [Cr^{Cl}_{(OH_2)_5} + H_2O]Cl_2,$$

the latter having two ionizable chlorine atoms and the former none.

The corresponding compounds in the case of the sulphate have been prepared and studied recently by Colson,[125] the results being in full accord with the theory of Werner.

The Theory of Abegg and Bodländer.[126, 127, 128] — (R. 128, p. 1.) "Man muss . . . bei anorganischen Verbindungen ausser von einer Affinität zwischen Atom und Atom noch von einer solchen zwischen Atom und elektrischer Ionenladung sprechen, welch letztere als *Elektroaffinität* bezeichnet werden möge.

"Die *Zersetzungsspannung* eines Ions, welche die elektromotorische Kraft angiebt, die zur Trennung der Ladung vom Ion aufgewendet werden muss, ist zwar kein genaues Maass für die *Elektroaffinität* des Ions, da sich keine isolierten Atome, sondern Molekeln abscheiden; sie giebt aber im Verein mit Betrachtungen über Löslichkeit und Dissociationszustand von Elektrolyten, sowie die Fähigkeit zur Komplexbildung ein annäherndes Maass für die Reihenfolge der Ionen nach ihrer Elektroaffinität. . . .

"Ich möchte nun ausführen, dass die *Komplexsalzbildung* mit der Elektroaffinität in nächstem Zusammenhange steht, und schicke dazu folgende Definition voraus:

"*Eine komplexe Verbindung ist eine solche, deren eines Ion aus einer Molekularverbindung zwischen einem einzeln existenzfähigen Ion ('Einzelion') und einer elektrisch neutralen Molekel ('Neutralteil') besteht.* . . .

"Besonders als Neutralteil geeignet ist das Wasser, und in der That spricht vieles dafür, dass die Ionen namentlich von geringer Elektroaffinität, und zwar sowohl Anionen als Kationen, hydratisiert sind. . . .

"Die Thatsache, dass die komplexen Ionen stärker als die Einzelionen sind, lässt folgende physikalische Erklärung zu:

"Durch die Neutralteiladdition wird das Volum und damit die Oberfläche des Ions vergrössert, so dass die pro Valenz stets gleiche Ionenladung auf dem Komplex ein geringeres elektrisches Potential erhält als auf dem Einzelion; das höhere Potential bedingt aber eine grössere Tendenz des Ions, sich zu entladen, die also durch Komplex-

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[125] Colson, Ann. chim. phys., **12**, 433 (1908).

[126] Abegg and Bodländer, "Die Elektroaffinität, ein neues Prinzip der chemischen Systematik," Z. anorg. Chem., **20**, 453 (1899).

[127] Abegg, "Die Valenz und das Periodische System. Versuch einer Theorie der Molekularverbindungen," *ibid.*, **39**, 330 (1904).

[128] Abegg, "Über Komplex Salze," Z. Electrochem., **6**, 92 (1899).

bildung verringert wird, was mit der grösseren Elektroaffinität gleichbedeutend ist."

An example of this occurs in the case of the alkali-ions, where, as we have seen (this review, Sec. II, p. 416), the degree of hydration increases in the series, K, Na, Li. According to Abegg and Bodländer (R. 126, p. 491), "Eine solche Verschiedenheit des Hydratationsgrades müsste ihrerseits nach den obigen Entwickelungen mit der verschiedenen Stärke der Ionen in Zusammenhang stehen, indem das schwächste Ion das grösste Additionsvermögen (= Bestreben, sich zu verstärken) besitzen wird. In der That ist das Lithium ein schwächeres Ion als Natrium, und das Kalium stärker als beide, was sich ohne Belege im einzelnen schon aus ihrem gesamten chemischen Verhalten bestätigt."

Abegg's views concerning the nature of the equilibria in a solution of an electrolyte are expressed as follows (R. 127, p. 359): "Ganz allgemein stellt eine Elektrolyt-Lösung nach unseren Anschauungen, . . . einen Gleichgewichtszustand zwischen folgenden Affinitäten dar:

"1. Ionen + Ionen $\rightleftarrows$ (undissoziierte Molekeln).

"2. Ionen + Lösungsmittel $\rightleftarrows$ (Ionen-Lösungsmittelverbindung).

"3. Undissoziierte Molekeln + Lösungsmittel $\rightleftarrows$ (deren Verbindung).

"Offenbar sind schlechtdissoziierende Lösungsmittel solche, die eine geringe Affinität (2) zu Ionen haben, und vice versa. Ist nun die Ionenbildungstendenz (1) eines Salzes stark, so muss die Affinität (3) seines undissoziierten Teils zum Lösungsmittels ohne wesentlichen Einfluss bleiben, da er im Verhältnis zu seinen Ionen keine hohen Konzentrationen erreichen kann. Diesen Fall repräsentieren die Lösungen aller starken Elektrolyte. Ihre Löslichkeit wird also wesentlich bestimmt durch die Affinitat ihrer Ionen zum Lösungsmittel, ist demgemäss gross in Wasser, gering in schwachdissoziierenden Medien."

Mention should also be made of certain other theories which involve hydration in solution as one of their deductions. Thus Euler[129] regards ammonium hydroxide as an amphotoric electrolyte and writes its formula, $H_3N \begin{matrix} \nearrow H^+ \\ \searrow OH^- \end{matrix}$; and from analogy thereto the formula for water is written, $H_2O \begin{matrix} \nearrow H^+ \\ \searrow OH^- \end{matrix}$, with one tetravalent oxygen atom. Carrying

[129] Euler, Arkiv. Kemi-Min. K. Svenska Veten.-Akad., Stockholm, 1, 203 (1904).

the analogy still further, he assigns to the silver-ammonia-ion and the silver-ion in aqueous solution the formulæ,

$$[Ag(NH_3)_2]^+ \text{ and } [Ag(H_2O)_2]^+.$$

Similarly the nickelous, cupric, and cobaltic ions in aqueous solution are assigned the formulæ,

$$[Ni(H_2O)_4]^{++}, \quad [Cu(H_2O)_4]^{++}, \text{ and } [Co(H_2O)_6]^{+++}.$$

In support of the formula assigned to the silver-ion the author adduces the following evidence. If the formula assigned to the silver-ion is correct, the addition of ammonia to a solution of silver nitrate simply results in the replacement of two water molecules by two ammonia molecules. The masses of the two ions are almost the same (143 and 141), and from the similarity in the structure of water and ammonia it is not unreasonable to suppose that the volumes are also nearly the same. The new ion ought, therefore, on this view, to have nearly the same equivalent conductance as the original silver-ion. The conductances are, according to Euler,

Silver-ion 51.8,

$[Ag(NH_3)_2]^+$ 52.0.

Similarly the viscosity coefficients of the two solutions should be nearly the same. They are given by Euler [130] as

¼ N. silver nitrate 1.018,

¼ N. $Ag(NH_3)_2NO_3$ 1.020.

Somewhat similar are the interesting views of Hantzsch [131] regarding the nature of ionization in solution. He regards an acid in solution as a "hydronium" salt, thus,

$$HCl + H_2O = [H_2O.H]Cl = (H_3O)^+ + Cl^-;$$

from analogy to the corresponding reaction by which an ammonium salt is formed from an acid and ammonia,

$$HCl + NH_3 = NH_3.HCl = (NH_4)^+ + Cl^-.$$

This last reaction corresponds to the process of ionization of an ammo-

[130] Compare, however, Blanchard's results (R. 120, p. 1330), which fail to confirm Euler's formulæ for the other ions when the same mode of reasoning is followed.

[131] Hantzsch, Z. physik. Chem., 61, 307 (1907).

nium salt in liquid ammonia, in which solvent the behavior of ammonium salts resembles the behavior of acids in aqueous solution, as shown by Franklin and Kraus.[132]

Mention may also be made of a recent paper by Lowry,[133] where the subject of electrolytic dissociation in general is discussed from the standpoint of a "solvate" theory.

The question of hydrated ions in its relation to the electron theory is considered briefly by Fournier-D'Albe.[134] According to the views of this author, when ionization takes place the two atoms separate, the negative atom or group taking one of the electrons from the positive atom or group. "The two ions so produced act as condensation nuclei, and each attracts molecules of the solvent about itself and becomes hydrated," the action resembling that which takes place in an ionized gas.

Hydration and Color Changes in Solution

Owing to the recent appearance of an excellent and exhaustive review of the subject of light absorption in solutions of electrolytes, under the authorship of G. Rudorf,[135] any attempt at an extended treatment of this phenomenon and of its relation to hydration in the present discussion would be superfluous. The reader who is interested in this phase of the subject should therefore refer to Rudorf's treatment, especially to pages 473–482 of Part I and to pages 390–411 of Part II. Since, however, this method has yielded one of the most satisfactory and conclusive *proofs* of the existence of hydrates in aqueous solution in certain instances, it seems desirable to include here a description of the experimental evidence and the theoretical interpretation which has led to this conclusion. This evidence is furnished by the experiments of Vaillant[136] and by those of Lewis[137, 138] on the color

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[132] Franklin and Kraus, Amer. Chem. J., **23**, 305 (1900).

[133] Lowry, "An Application to Electrolytes of the Hydrate Theory of Solutions," Trans. Farad. Soc., **2**, 197 (1905).

[134] Fournier-D'Albe, "The Application of the Electron Theory to Electrolysis," Chem. News, **95**, 28 (1907); Engineering, **83**, 87 (1907).

[135] G. Rudorf, Jahb. Rad. u. Elec., **3**, 422 (1907), and **4**, 380 (1908).

[136] Vaillant, Ann. chim. phys. [7], **28**, 257 (1903).

[137] Lewis, Z. physik. Chem., **52**, 224 (1905); also

[138] Bureau of Gov. Lab's P. I. Pub. No. **30**, 21 (1905).

changes produced in solutions of cobalt and copper salts by the addition of a second solute to the solution. The experiments of Vaillant, while no less conclusive, do not furnish so direct and simple a demonstration of the point in question as do those of Lewis, which we shall therefore consider here.

The changes in color undergone by solutions of cobalt and of copper salts when they are diluted were attributed by Wiedemann [139] to the gradual hydration of the salts. This explanation was later succeeded by that of Ostwald, according to which the color changes were attributed to ionization, the ions and undissociated molecules being supposed to have different colors. More recently Donnan and Basset [140] and Kohlschütter [141] have shown the presence of colored complex ions (such as $CoCl_4^{--}$, for example) in these solutions, and the color changes taking place on dilution were attributed by Donnan to the formation and dissociation of these complex ions. Lewis has shown that neither of these last two theories is alone sufficient to explain the facts, but that water enters into the reaction which produces the color change.

According to the three different explanations we should have,[142] respectively, equilibria of the following three types existing in the solution:

$$CuBr_2 \text{ (brown)} \rightleftharpoons Cu^{++} \text{ (blue)} + 2Br^{-}. \qquad (a)$$

$$CuBr_4^{--} \text{ (brown)} \rightleftharpoons CuBr_2 \text{ (blue)} + 2Br^{-}. \qquad (b)$$

$$CuBr_2 \text{ (brown)} + nH_2O \rightleftharpoons Cu(H_2O)_n^{++} \text{ (blue)} + 2Br^{-}. \qquad (c)$$

The color change in the last case may of course be due chiefly, not to a change from the anhydrous undissociated salt to the hydrated ion, but to a change from a hydrate with less water to one with more; but in any case the argument would be the same, so we may assume the above reaction for the sake of simplicity.

According to equations (*a*) and (*b*), the Mass-Action Law requires that the equilibrium between the brown and the blue constituents shall, at constant temperature, depend only upon the concentration of the bromide-ion. According to the equation (*c*), however, the equilibrium depends not only upon this factor but also upon the active mass of

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[139] Wiedemann, Report Brit. Assoc., p. 346 (1887).

[140] Donnan and Basset, Trans. Chem. Soc., 81, 939 (1902).

[141] Kohlschütter, Ber. Chem. Ges., 37, 1168 (1904).

[142] See Lewis, Z. physik. Chem., 56, 223 (1906).

the water. In order to decide between these two hypotheses, Lewis (R. 138, p. 25) made the following series of experiments: "The same quantity of cupric bromide was added to 10 c.c. of a thrice-normal solution of each of the following bromides, KBr, NH_4Br, NaBr, LiBr. In these solutions the concentrations of bromide-ion are nearly alike, being somewhat greater in the case of KBr, somewhat less in the case of LiBr. If this were the only factor determining the color, we should expect the solution in KBr to be the most brown, that in LiBr the least.

"The facts are just the opposite. The NH_4Br and NaBr solutions have nearly the same color, that of KBr is less brown, while the LiBr solution is very much browner. In all these solutions the blue is so faint, as compared with the brown, that the relative brownness of the solutions can be found by means of a colorimeter. Columns of LiBr, NaBr, and KBr solutions, respectively 14, 18.5, and 20 mm. thick, appeared equally brown.

"These experiments were repeated several times, a different quantity of cupric bromide being used in each instance. The results were the same. A small change in the concentration of cupric bromide in any solution changes only the density of the color, but not its character. It is obvious that something influences the color besides the concentration of the bromide-ion. . . .

"Similar experiments were made with cupric chloride and solutions of the five chlorides, KCl, NH_4Cl, NaCl, LiCl, and HCl. Here the colors are not so pronounced as in the previous case. All the solutions are green. No difference could be detected in the first three, but the LiCl solution was decidedly greener and the HCl solution still more so." When the chlorides of the alkaline earth metals were used, the influence upon the color was found to be much greater, the order being $SrCl_2$, $CaCl_2$, $MgCl_2$, $BeCl_2$.

"All these experiments were repeated, using cobaltous chloride in place of cupric. The color differences here are less marked. The solutions of the chlorides of the first group all had practically the same red color with a tinge of blue. But in the second group the solutions were a more decided purple and arranged themselves in the same order as before, that is, $BeCl_2$ gave the solution with most blue in it."

As regards their relative effects upon the color changes, therefore, these various salts arrange themselves in the same order as is exhibited by their effects upon the activity (active-mass) of the water, as we have seen in Section I, page 364. Since, therefore, changes in color are

produced when the activity of the water alone is changed, we must conclude that water enters into the reaction which causes the color change. This result, taken in conjunction with the experiments of Donnan and Basset, referred to above, renders it probable that equilibria of the following type exist in solutions of cobalt and copper salts.

$$\underset{red}{CoCl_2(H_2O)_n} + mCl^- \rightleftharpoons [\underset{blue}{CoCl_2(Cl)_m}(H_2O)_p]^{(m)-} + (n-p)H_2O.$$

Kohlschütter (R. 141, p. 1168), in conformity with Werner's theory, expresses the reaction producing the color change in copper chloride solutions as follows:

$$[Cu^{Cl}_{(H_2O)_2}]^+ + H_2O \rightleftharpoons [Cu(H_2O)_4]^{++} + Cl^-.$$

These formulæ are based upon the analogy with the corresponding ammonia complexes, whose existence has been demonstrated, copper being assigned the coördination number, 4.

The Effect of Salts upon Reaction Velocities in Aqueous Solution

In a recent investigation R. J. Caldwell[143] has shown that the velocity of the inversion of cane sugar by acids in aqueous solution is, for a given strength of acid, much more nearly proportional to the concentration of the sugar if the concentration is expressed as mols per 1,000 grams of water instead of as mols per liter of solution. Employing, therefore, the weight-normal method of expressing concentration, he studied the effect of various chlorides upon the velocity of inversion of cane sugar by hydrochloric acid, and found in each case a marked acceleration in the rate of the inversion. To explain this phenomenon the author assumes that the salt is hydrated in solution, and thus by the removal of a portion of the water from its rôle as solvent exerts a "concentrating effect" upon the sugar; hence the acceleration in the rate of inversion. To determine the "average hydration" for the salt in question, it is only necessary, according to the author, to find by experiment how much water must be added to the solution containing the salt in order to restore the velocity constant to its original value. The author does this for a number of chlorides and obtains the results shown in Column II of Table XVIII.

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[143] Caldwell, Proc. Roy. Soc., London, 78, 290 (1906).

TABLE XVIII

"AVERAGE HYDRATION" OF SALT

Salt added.	I. Me. Ac.	II. Sugar.
KCl	8 H_2O	10 H_2O
NH_4Cl	5 H_2O	10 H_2O
NaCl	10 H_2O	13 H_2O
$BaCl_2$	18 H_2O	19 H_2O
$CaCl_2$	20 H_2O	22 H_2O
CH_3COOH	..	1 H_2O
$AgNO_3$	..	5 H_2O
NH_4NO_3	−2 H_2O	7 H_2O
KNO_3	1 H_2O	8 H_2O
$NaNO_3$	3 H_2O	11 H_2O
$LiNO_3$	..	13 H_2O
$SrNO_3$	5 H_2O	18 H_2O
$CaNO_3$	7 H_2O	..

R. Wymper [144] has recently made a similar investigation of the effect of nitrates upon the rate of inversion of cane sugar solutions by nitric acid. His results also appear in Table XVIII, Column II. In both of these investigations the concentration of the salt was about 1 mol per 1,000 grams of water. The effects of certain nonelectrolytes were also studied by these investigators. Glycerol and, to a greater degree, ethyl alcohol were found to exert a marked retardation upon the rate of inversion, while milk sugar was found to be practically without effect.

This work was still further extended by H. E. Armstrong and J. A. Watson,[145] who studied in a similar manner the effects of salts upon the rate of the hydrolysis of methyl acetate by hydrochloric and nitric acids. They found an acceleration in most cases in the presence of the salt and attributed it to the hydration of the salt. Their values for the "average hydration" of the various salts investigated are shown in Column I of Table XVII. The effects of the initial presence of the products of the hydrolysis — methyl alcohol and acetic acid — were also tried, and the former found to be practically without effect, while the latter had a distinctly accelerating action.

[144] Wymper, Proc. Roy. Soc., London, 79, 576 (1907).

[145] Armstrong and Watson, Proc. Roy. Soc., London, 79, 586 (1907).

To this same class belongs the recent investigation of E. H. Rennie, A. J. Higgin, and W. T. Cooke,[146] who studied the effect of the presence of various nitrates upon rate of solution of copper in nitric acid. Of the nitrates studied, that of sodium, and to a greater degree that of lithium, was found to exert a marked accelerating effect upon the rate of solution. Potassium nitrate was without effect, while cæsium and rubidium nitrates retarded the rate of solution. Beginning, therefore, with the nitrate producing the greatest acceleration, these salts arrange themselves in the following order: Li, Na, K, Rb, Cs. The order is here the same as found by Wymper for the effects of these salts upon the rate of inversion of cane sugar, and is attributed by the authors to the same cause, namely, the "concentrating effect" exerted by the salts in virtue of their hydration. The authors conclude that "these results afford additional evidence that the process of solution is accompanied by the combination of the solute with the solvent."

Without in any way questioning the importance of the investigations just described or of the value of the data obtained,[147] it is scarcely possible to agree with the interpretation placed by the investigators upon their results. Although several theories have been advanced to explain the neutral-salt-action, the question is still very much an open one, and the accumulation of further accurate data in this field is very desirable; but it is scarcely probable that it will ever yield *reliable* evidence concerning the complexity, or even the existence, of hydrates in aqueous solution. We have already noted and discussed (see Section I) the difficulties in the way of using an *equilibrium* (even in a *homogeneous binary* system) for the purpose of studying hydration in solution. In the method just considered the authors propose, however, to use the *rate* of a reaction and that in a *three-component* (and in the last instance even a *heterogeneous*) system as a basis not only for studying relative hydrations in solution, but even for calculating the complexity of such hydrates.

Conclusion

In concluding this review it seems desirable to emphasize again certain of the more important features. When we examine the various

[146] Rennie, Higgin, and Cooke, J. Chem. Soc., 93, 1162 (1908).

[147] Compare, however, Senter [Trans. Farad. Soc., 3, 163 (1907)], who, from his own experiments and from those of Arrhenius, Spohr, Kay, and others, finds that "the accelerating effect of neutral salts is practically independent of the nature of the salt."

methods which have been applied to the solution of this question, we find three methods which are distinguished from the rest by their freedom from arbitrary assumptions, and whose results are therefore to be regarded as constituting definite proof of the existence of hydrates in aqueous solutions.

(1) One of these is the solubility method. The existence of a solid hydrate in equilibrium with its solution is conclusive proof that the same compound is present in the solution. We have seen, moreover, that the shape of the solubility or melting-point curve is a fair indication of the stability of the compound in the liquid phase. This method is restricted to a definite hydrate in each instance, and so far as any quantitative conclusions are concerned it is necessarily confined to saturated and very concentrated solutions. At present it does not appear to be capable of further development on the quantitative side, except possibly in certain instances where the solute is found to exhibit a "maximum rate of solution."

(2) Certain copper and cobalt salts in aqueous solution undergo color changes when the solution is diluted. We have seen that the water enters into the reactions which produce these color changes. The solute is consequently hydrated in solution. This method is necessarily restricted to a few cases, and has not yielded any results of a quantitative nature.

(3) The third method deals with the hydration of ions in aqueous solution and is based upon transference measurements. This method is superior to either of the others, because it can be applied to a large number of solutions at different concentrations and temperatures, and because it yields quantitative results on the relative degrees of hydration of the ions. When carried out in the manner indicated (*i.e.*, by combining Hittorf transference numbers with those obtained by the method of moving boundaries) it offers a most promising field for future research (R. 120*a*).

In addition to these three methods, there exists, as we have seen, a large number of methods, the results of which, taken individually, cannot be regarded as conclusive, owing to certain assumptions which they involve. Taken together, however, and in conjunction with the three methods above mentioned, they constitute a strong body of evidence concerning the existence and nature of complexes between solute and solvent in solution. Of these methods the one which promises the most for future investigation is the method depending upon the lower-

CONTRIBUTIONS FROM THE
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
No. 39

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS[1]

PART IV. ANALYSIS OF THE ALKALINE-EARTH AND ALKALI GROUPS

BY WILLIAM C. BRAY

INTRODUCTION

THE earlier parts of this system of analysis have dealt with the "Preparation of the Solution,"[2] the "Analysis of the Silver, Copper, and Tin Groups,"[2] and the "Analysis of the Aluminum and Iron Groups."[3] The present part treats of the analysis of the two remaining groups of metallic elements, which include barium, strontium, calcium, magnesium, sodium, potassium, and the rarer element, lithium. The general purposes of the investigation, the method of presentation, and the meaning of the abbreviations used have been described in the Introduction to the first paper.[2]

GENERAL DISCUSSION

In the method of analysis here presented magnesium is precipitated by ammonium carbonate, together with the other alkaline-earth elements (barium, strontium, and calcium), instead of being separated from them by this reagent. This somewhat radical modification of the usual process was made possible by the knowledge that magnesium separates out completely as a double ammonium magnesium carbonate when the solution is cold, and is concentrated with respect

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[1] Copyright, 1909, by ARTHUR A. NOYES.

[2] A. A. Noyes and W. C. Bray, this QUARTERLY, **19**, 191 (1906).

[3] A. A. Noyes, W. C. Bray, and E. B. Spear, this QUARTERLY, **21**, 14 (1908).

to both ammonium carbonate and ammonium hydroxide (the effect of the latter substance being to drive back the hydrolysis of the ammonium carbonate). Some time is, to be sure, required for complete precipitation, but this may be reduced from several hours to less than half an hour by the addition of alcohol. This method was developed in connection with experiments that were made to determine the proper conditions for precipitating calcium, strontium, and barium completely, in the course of which it was found not possible to attain this result by increasing the concentration of the ammonium carbonate without at the same time causing the precipitation of magnesium when much was present. It was, however, afterwards found that Schaffgotsch,[1] as early as 1858, had recommended this method of separating magnesium quantitatively from the alkali elements, and an improved process has been recently described by Gooch and Eddy[2] which is almost identical with that devised in the present work.

One of the great advantages of this process is that the precipitation of calcium, strontium, and barium as carbonates is much more complete than in the usual method, where only a small quantity of ammonium carbonate is added, and where, to detect and remove these elements, it is necessary to add ammonium sulphate and ammonium oxalate to the filtrate. The process also makes unnecessary the lengthy operation of removing magnesium before testing for the alkali elements, which involves ignition to remove ammonium salts, precipitation of magnesium hydroxide by barium hydroxide, and subsequent removal of the barium. The only disadvantages of the process are that about half an hour is required to complete the precipitation of magnesium and that a somewhat longer time is required for filtration than when the carbonates are precipitated from a hot solution. These, however, seem slight in comparison with the lack of delicacy of the ordinary process of precipitation and the difficulty of subsequently removing magnesium.

In the analysis of the alkaline-earth group the ammonium carbonate precipitate is dissolved in acetic acid, and barium and strontium are precipitated as chromates, the former from an acetic acid solution of known concentration, the latter by making the filtrate alkaline with ammonia and adding alcohol. This method of precipitating barium

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[1] Ann. Physik., 104, 482 (1858).

[2] Am. J. Sci., [4], 25, 444 (1908); Z. anorg. Chem., 59, 427 (1908).

has been adopted in nearly all text-books in qualitative analysis, and the precipitation of strontium as chromate has been recommended by a few authors.[1] I was, however, found necessary to carry out a large number of experiments to determine the conditions under which a small amount of either element is easily detected and a large amount completely precipitated, and under which a large quantity of strontium, when present alone, does not interfere with the test for barium, and a large quantity of calcium does not interfere with that for strontium. This portion of the investigation was carried out by Dr. E. B. Spear in this laboratory.

After barium and strontium have been thus removed, calcium is precipitated as calcium oxalate, the filtrate is made strongly ammoniacal, and the magnesium precipitated by adding sodium phosphate and alcohol. In order to prevent the precipitation of some magnesium as oxalate when much of it is present, it is necessary to dilute the solution to about 300 ccm. before making the test for calcium; but this large volume does not prevent the detection of even less than 1 mgm. of magnesium. It may seem remarkable that the precipitation of magnesium ammonium phosphate is such a delicate test under these conditions, especially in view of the fact that it is usually directed to make the precipitation in as small a volume as possible. The difference is brought about by the presence in the solution of a moderate amount (about 20 per cent.) of alcohol, which doubtless greatly decreases the tendency of the solution to remain supersaturated.

The filtrate from the ammonium carbonate precipitate, which should now contain only salts of the alkali elements, is evaporated to dryness; the ammonium salts are expelled by ignition, and the residue dissolved in a little water. This solution is divided into two parts; the smaller one is tested for lithium and potassium, and the larger for sodium. Lithium is precipitated as phosphate from a hot, slightly alkaline solution, the delicacy of the test being greatly increased by the addition of a little alcohol. The potassium is tested for in the filtrate, after expelling the alcohol completely, by adding sodium cobaltinitrite, which gives a precipitate of $K_2NaCo(NO_2)_6H_2O$. This reaction has been used as a quantitative method of determining potassium;[2] it is delicate

[1] W. Fresenius and F. Ruppert, Z. analyt. Chem., 30, 677 (1891). Caron and Raquet, Bull. soc. chim. [3], 35, 1061 (1906).

[2] Adie and Wood, J. Chem. Soc., 77, 1076 (1900). Drushel, Am. J. Sci. [4], 24, 433 (1907); 26, 329 (1908).

enough to enable 0.2–0.3 mgm. of potassium to be detected in 5 ccm. of solution. In order to detect sodium the second portion of solution is evaporated and treated with an alkaline potassium pyroantimonate solution.[1] When the reagent is properly prepared this test is satisfactory and reliable on account of the characteristic appearance of the crystals of sodium pyroantimonate formed, and it is delicate enough to detect 1 or 2 mgm. of sodium in the portion of solution tested. It is seldom that a more delicate test for this abundant element is necessary; indeed, if a much more sensitive one be employed, the sodium introduced in the process of analyses from the reagents, the glass vessels, and the dust of the air would prevent a blank being obtained in the absence of this element. For this reason, and because it gives no idea of the quantity present, the flame test relied upon in some schemes of analyses is unsatisfactory. Unfortunately, however, the presence of a large amount of a potassium salt prevents the precipitation of even several milligrams of sodium; moreover, even a small amount of lithium gives a similar precipitate. In these cases, before making the test for sodium, the lithium is removed by precipitating it as fluoride, and the potassium is greatly reduced in quantity by precipitating a large part of it as sulphate.

An as yet unpublished scheme of analysis for the alkali elements, which included also rubidium and cæsium, was worked out a few years ago in this laboratory by A. A. Noyes and J. E. Ober. In the first step of the process, following the method in common use, sufficient chlorplatinic acid was added to convert all the elements into the corresponding chlorplatinates; the sodium and lithium salts were washed out by means of alcohol, and the potassium, rubidium, and cæsium salts left undissolved. In the present scheme, in which the detection of the common elements is of primary importance, this process has not been adopted on account of the time required to make this separation and to remove the platinum before testing for sodium and lithium, and also on account of the expense involved in the use of the large amount of chlorplatinic acid required.

A final confirmatory test is given for each element except magnesium. These tests will be omitted by the experienced analyst except when a small precipitate or one of doubtful character is obtained. The test for calcium is made by treating the oxalate precipitate with dilute

[1] Cf. Boettger, Qualitative Analyse, Zweite Auflage, 232.

sulphuric acid, and precipitating the calcium sulphate from the solution by the addition of alcohol. The test for strontium depends on the transformation of the strontium chromate into carbonate at 100° in a solution containing sodium carbonate and sufficient oxalate to transform any calcium salt present into oxalate; the strontium is dissolved in acetic acid and precipitated by adding ammonium hydroxide and carbonate, and boiling. The presence of the remaining elements is confirmed by the usual flame tests. The confirmatory tests for calcium, strontium, barium, and lithium can be made in a still more satisfactory manner by the use of a small "pocket" spectroscope, comparative experiments being made with known solutions. A small instrument of this kind, which costs less than a platinum dish, should be available in every laboratory of qualitative analysis because of the educational value to the student.

Tabular Outline

In Table X an outline of the process is given, the confirmatory tests being, however, omitted. The symbols of the anhydrous substances are given without reference to the actual state of hydration of the precipitates. When lithium is not to be tested for, the directions enclosed within brackets are to be omitted. No attempt should be made to carry out an analysis without consulting the detailed directions given in the Procedures.

TABLE X — ANALYSIS OF THE ALKALINE-EARTH AND ALKALI GROUPS

Solution containing Ba, Sr, Ca, Mg; Li, K, Na.

Evaporate to a small volume, add $(NH_4)_2CO_3$ *and alcohol, filter after ½ hour (P. 81).*

<table>
<tr><td colspan="3">Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$.$(NH_4)_2CO_3$.
Dissolve in acetic acid, add K_2CrO_4 (P. 82).</td><td colspan="3" rowspan="2">Filtrate. Evaporate, ignite, add 5–10 ccm. water (P. 91).</td></tr>
<tr><td rowspan="4">Precipitate:
$BaCrO_4$.</td><td colspan="2">Filtrate. Add NH_4OH and alcohol (P. 84).</td></tr>
<tr><td rowspan="3">Precipitate:
$SrCrO_4$.</td><td colspan="2">Filtrate. Dilute, add $(NH_4)_2C_2O_4$ (P. 86).</td><td rowspan="3">To one-third of solution [add NaOH and Na_2HPO_4, heat, add alcohol (*P. 91a)].</td><td rowspan="3">Remainder. [Precipitate Li as LiF (P. 94)].
Evaporate to 1 ccm., add $K_2H_2Sb_2O_7$ reagent (P. 94).</td></tr>
<tr><td>Precipitate:
CaC_2O_4.</td><td>Filtrate.
Add NH_4OH and Na_2HPO_4 (P. 88).</td></tr>
<tr><td>Precipitate:
$MgNH_4PO_4$.</td><td>Precipitate:
Li_3PO_4.</td><td>Solution.
Add $Na_3Co(NO_2)_6$ (P. 92).
Precipitate:
$K_2NaCo(NO_2)_6$.</td><td>White crystalline precipitate:
$Na_2H_2Sb_2O_7$.</td></tr>
</table>

Procedures and Notes

Alkaline-Earth Group

Procedure 81. — Evaporate the filtrate from the NH_4OH and $(NH_4)_2S$ precipitate (P. 51) to a volume of about 10 ccm., and filter off any sulphur that may have precipitated. To the cold solution add 30 ccm. of the $(NH_4)_2CO_3$ reagent (see N. 2) and 30 ccm. 95% alcohol; let the mixture stand for at least half an hour, shaking frequently. (Precipitate, presence of ALKALINE-EARTH ELEMENTS.) Filter and wash the precipitate with a little of the $(NH_4)_2CO_3$ reagent; if the precipitate is large, dry it by suction. (Precipitate, P. 82; filtrate, P. 91.)

Notes.—1. The filtrate from the $(NH_4)_2S$ precipitate should be colorless or light yellow (see P. 51, N. 12). It is evaporated in order that the elements of the alkaline-earth group may be precipitated more quickly and more completely. The volume to which the $(NH_4)_2CO_3$ reagent is added should not exceed 20 ccm. The evaporation also serves to destroy $(NH_4)_2S$ and to coagulate any sulphur that may separate.

2. The reagent used in precipitating the elements of this group is conveniently prepared by dissolving 100 grams freshly powdered ammonium carbonate in 300 ccm. NH_4OH (0.96), filtering if there is any precipitate, and adding 100 ccm. NH_4OH (0.90). The solid carbonate contains a large proportion of ammonium carbamate, $NH_2CO_2NH_4$; but, on dissolving, the latter is rapidly converted into ammonium carbonate.

3. In an ammoniacal ammonium carbonate solution, calcium, strontium, and barium are precipitated as carbonates. If the ammonium carbonate and hydroxide were added in only small excess, the precipitation would not be complete, and additional tests for these elements would have to be made (for example, by adding to the filtrate $(NH_4)_2C_2O_4$ and $(NH_4)_2SO_4$). But by the use of a concentrated solution of $(NH_4)_2CO_3$, and the addition of a large excess of NH_4OH to diminish the hydrolysis of the carbonate into $(NH_4)^+HCO_3^-$ and NH_4OH, the precipitation may be made practically complete, owing to the greatly increased concentration of the carbonate ion (CO_3^{--}).

4. When the concentrations of $(NH_4)_2CO_3$ and NH_4OH are sufficiently great, magnesium is in the cold also quantitatively precipitated as a double carbonate, $MgCO_3.(NH_4)_2CO_3.4H_2O$. This substance is, however, fairly soluble in water, and the solubility increases rapidly with the temperature.

5. In an aqueous solution in the cold, the precipitation of these ele-

ments takes place slowly, especially in the case of magnesium and calcium, but it is greatly accelerated by the addition of alcohol and by shaking. Under the conditions recommended in the procedure, not more than 0.1–0.3 mgm. of any of the four elements remains in solution after half an hour, and even 0.5 mgm. is easily detected within this time.

6. Li_2CO_3 is by far the least soluble carbonate of the alkali elements, but under the conditions of the procedure no precipitate is obtained, even when 150 mgm. of lithium are present. Larger amounts of lithium yield a precipitate; but this case will seldom, if ever, occur if the weight of the original substance taken for analysis did not exceed 1 gram. The presence of the alkali elements does not interfere in the analysis of the alkaline-earth group, and it is therefore not necessary to wash the $(NH_4)_2CO_3$ precipitate.

Procedure 82. — Dissolve the $(NH_4)_2CO_3$ precipitate (P. 81) by pouring repeatedly through the filter a portion of hot dilute acetic acid (10–25 ccm. 30% acid). Make the solution slightly alkaline with NH_4OH; add 30% acetic acid, drop by drop, until the solution after shaking is just acid to litmus, and then add 3 ccm. more. Dilute to 40 ccm., heat just to boiling in a flask; measure out 10 ccm. 20% K_2CrO_4 solution and add it a few drops at a time; if a precipitate forms, heat the mixture just to boiling and shake it after each addition; finally, heat the mixture at 90–100° for 1 or 2 minutes, shaking it frequently. Filter, even though the solution appears clear; remove the filtrate, and wash the precipitate thoroughly with cold water. (Pale yellow precipitate, presence of BARIUM.) (Precipitate, P. 83; filtrate, P. 84.)

Notes.— 1. The solubility in water of the chromates of the alkaline-earth elements increases rapidly in the order, Ba, Sr, Ca, Mg. The difference in solubility of $BaCrO_4$ and $SrCrO_4$ is so great that under the conditions of the procedure 0.5 mgm. Ba can be detected, while even 400 mgm. Sr give no precipitate. The amount of K_2CrO_4 added is sufficient to precipitate completely more than 500 mgm. of barium.

2. Acetic acid is added to prevent the precipitation of $SrCrO_4$. By its action the concentration of the chromate-ion is reduced, owing to its conversion into hydrochromate-ion and bichromate-ion, according to the reactions:

$$2CrO_4^{--} + 2H^+ = 2HCrO_4^- = H_2O + Cr_2O_7^{--}.$$

The relative amounts of these two ions present in the acid solution

depend upon the dilution; in the fairly concentrated solution used in this procedure $Cr_2O_7^{--}$ predominates, but this would be reversed in a much more dilute solution. Since $HCrO_4^-$ is a weaker acid than acetic acid, the CrO_4^{--} concentration in the acid solution is very small. It is evident that the CrO_4^{--} concentration decreases as the H^+ concentration increases. For this reason the presence of excess of a strong acid (such as HCl or HNO_3 in the absence of acetate) prevents the precipitation of $BaCrO_4$; but owing to the fact that acetic acid is itself a weak acid, and that a large amount of acetate is present, the addition of a considerable excess of acetic acid has but little effect. The most satisfactory separation of barium and strontium is obtained when a small excess of acetic acid is present; 2 ccm. 30% acetic acid is nearly equivalent to 10 ccm. 20% K_2CrO_4 solution.

3. The K_2CrO_4 is added slowly to a hot solution; the mixture is shaken and heated in the neighborhood of 100° before filtering, since otherwise the precipitate is liable to pass through the filter. By this method of precipitation almost all the barium is precipitated before an excess of K_2CrO_4 is added; this is of special importance when much barium is present, since as much as 3 mgm. Sr may then be carried down completely if the K_2CrO_4 reagent is added quickly. If for any reason the filtrate is turbid after two or three filtrations, the precipitate ($BaCrO_4$) may be coagulated by boiling gently for 1 or 2 minutes. Vigorous or long-continued boiling is to be avoided, since, owing to loss of acetic acid, $SrCrO_4$ may then separate if much strontium is present. The presence of 1 mgm. or more of barium is indicated by a distinct turbidity or the formation of a precipitate; when the amount is smaller than 1 mgm. it is very difficult to distinguish the faint turbidity in the colored solution, and the pale yellow precipitate can be seen only after filtering and washing the K_2CrO_4 out of the filter. The precipitate must always be washed thoroughly, in order to remove strontium as completely as possible, which otherwise would obscure the confirmatory test for barium in P. 83.

Procedure 83. — To confirm the presence of barium dissolve the K_2CrO_4 precipitate (P. 82), or a portion of it, in HCl (1.12), and evaporate the solution to a few drops. Dip a clean platinum wire into the solution, and introduce the wire into a colorless flame. (Green flame, presence of BARIUM.)

Note. — HCl is used, instead of HNO_3, in dissolving the precipitate, because the flame test for barium is then somewhat more delicate, owing

to the greater volatility of the chloride. When the amount of barium is very small, only a momentary green color is seen as the yellow (sodium) color which first appears fades away. The presence of chromium does not interfere with the test.

Procedure 84. — To the filtrate (P. 82), after cooling it, add NH_4OH (0.90) slowly until the color of the solution changes from orange to yellow, and then 3 ccm. more. Dilute the solution to 60 ccm., and add slowly, with constant shaking, 50 ccm. 95% alcohol. (Pale yellow precipitate, presence of STRONTIUM.) Filter after several minutes, using suction if filtration is slow; but do not wash the precipitate. (To ensure the complete precipitation of strontium, when much strontium or barium has been found, add to the filtrate 5 ccm. 20% K_2CrO_4 solution and 10 ccm. alcohol; filter off any precipitate that separates, and reject it if a precipitate has already been obtained in this procedure.) (Precipitate, P. 85; filtrate, P. 86.)

Note.— Under the conditions of the procedure, 0.5 mgm. of strontium is detected almost at once, and a smaller amount on standing: while even 400–500 mgm. of calcium or magnesium give no precipitate. A moderate change in the conditions will not affect this result; but if the concentration of alcohol or K_2CrO_4 is much less than is recommended, the precipitation of strontium may be incomplete; while the addition of larger amounts of alcohol and K_2CrO_4 may cause the precipitation of chromate of calcium or magnesium if much of these elements is present, or of K_2CrO_4 itself, since the latter is not very soluble in alcohol. The confirmatory test should therefore be tried. The precipitate is not washed, because $SrCrO_4$ is a fairly soluble substance.

Procedure 85. — To confirm the presence of strontium, transfer the precipitate (P. 84) (or a portion of it if the precipitate is large), with the filter if necessary, to a casserole; add a mixture of 30–35 ccm. 3% $Na_2C_2O_4$, 2 ccm. 10% Na_2CO_3 (both measured out in graduates), and about 0.5 ccm. 20% K_2CrO_4; cover the casserole with a watch glass, heat to boiling, and boil gently for 3–5 minutes. Filter, wash the precipitate thoroughly with water, pour repeatedly through the filter about 5 ccm. of 5% acetic acid; add to this solution NH_4OH in excess and 3–5 ccm. of the $(NH_4)_2CO_3$ reagent; heat to boiling in a small flask and set aside for 5–10 minutes. (White precipitate, presence of STRONTIUM.)

Notes.—1. In a boiling solution containing oxalate and carbonate in the proportions recommended in the procedure, small quantities of calcium and strontium are converted in a few minutes almost quantitatively into oxalate and carbonate, respectively. At 100° the solubility-product of calcium oxalate is not more than 1.5 times as great as that of calcium carbonate, and therefore the carbonate will be converted into the oxalate when the ratio of the concentrations of $Na_2C_2O_4$ and Na_2CO_3 is greater than this amount. The ratio adopted in the procedure is about 4 to 1. In the case of strontium, however, the oxalate is so much more soluble than the carbonate that even when this ratio is as great as 8 to 1 no strontium oxalate is formed. To provide for the very rare case that barium is present, a small amount of K_2CrO_4 is added; the barium then remains as $BaCrO_4$, the yellow color of which is easily seen on the filter after washing out the K_2CrO_4. In this procedure it will usually be more convenient to prepare a special reagent by dissolving 30 grams $Na_2C_2O_4$, 6 grams Na_2CO_3, and about 3 grams K_2CrO_4, and diluting the mixture to 1 liter.

2. In the treatment with dilute acetic acid the strontium is dissolved, but not enough calcium to give a test with ammonium carbonate. If barium is present, a little $BaCrO_4$ dissolves, giving a yellow solution; it may, however, be easily removed by adding excess of K_2CrO_4 and boiling the acid solution (see P. 82).

3. In this procedure the presence of 0.5 mgm. of strontium may be detected, and a perfect blank is obtained even with 30 mgm. of calcium or magnesium. With larger amounts of calcium, however, a very small precipitate may be obtained with ammonium carbonate.

4. If a spectroscope is available, the presence of strontium in the precipitate obtained in P. 84 may be quickly detected, after dissolving the precipitate in a little nitric acid and evaporating the solution to a few drops. Comparative tests with pure strontium and calcium solutions should be made.

Procedure 86. — To the filtrate (P. 84) add 200 ccm. water; heat to boiling, and add slowly to the boiling solution 20–50 ccm. 4% $(NH_4)_2C_2O_4.H_2O$ solution; shake, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.) Filter, and wash the precipitate once with water. (Precipitate, P. 87; filtrate, P. 88.)

Note.—The solution is heated to boiling, the ammonium oxalate is added slowly, and the mixture is allowed to stand a few minutes, since

otherwise the filtration is slow and calcium oxalate may pass through the filter. Moreover, since small amounts of calcium do not precipitate rapidly in the cold, 2 or 3 mgm. may escape detection if the mixture is not heated. Under the conditions of the procedure, *i. e.*, in a volume of about 300 ccm., 0.5 mgm. of calcium can be detected within 5 minutes, while 400 mgm. of magnesium give no precipitate. If, however, the volume of the solution is much less than 300 ccm. and much magnesium is present, some may precipitate, especially if the mixture be allowed to cool to room temperature.

Procedure 87. — Dissolve the $(NH_4)_2C_2O_4$ precipitate (P. 86), or a portion of it, in 5 ccm. cold, dilute H_2SO_4 (1.20); filter if necessary; add 10–15 ccm. 95% alcohol, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.)

Notes.—1. $CaC_2O_4.H_2O$ is very difficultly soluble in water, but dissolves in dilute solutions of highly ionized acids, owing to the formation by metathesis of un-ionized $HC_2O_4^-$. $CaSO_4$ is somewhat soluble in dilute H_2SO_4, but is completely thrown out as a flocculent precipitate by the addition of 2 or 3 volumes of alcohol. 1 mgm. of calcium gives a distinct turbidity at once, 0.5 mgm. in 1–3 minutes, and 0.2 mgm. within 10 minutes.

2. Moderate amounts of magnesium and of K_2CrO_4 do not interfere with this test, and it is therefore unnecessary to wash the precipitate thoroughly in P. 86. If strontium is present, however, a small amount of it dissolves in the H_2SO_4 and gives a slight turbidity at once on the addition of alcohol, corresponding to that given by only 0.2–0.3 mgm. of calcium after standing a few minutes. Therefore anything more than a slight turbidity is a conclusive proof of the presence of calcium.

Procedure 88. — To the filtrate from the $(NH_4)_2C_2O_4$ precipitate (P. 86) add 10 ccm. NH_4OH (0.90) and 20 ccm. 10% $Na_2HPO_4.12H_2O$ solution; cool, and shake the mixture; if no precipitate forms, let the mixture stand for at least half an hour, shaking it frequently. (White precipitate, presence of MAGNESIUM.)

Note.—This test for magnesium depends upon the precipitation of magnesium ammonium phosphate, $Mg^{++}(NH_4)^+PO_4^{---}$. This salt is somewhat soluble in water, owing chiefly to hydrolysis into NH_4OH and $Mg^{++}HPO_4^{--}$; and the test is therefore made in a strongly ammoniacal solution. Since the solubility increases rapidly with the temperature,

the solution is cooled to the room temperature, or below. In an aqueous solution this substance shows a great tendency to form a supersaturated solution, and it is therefore usually directed to make the test in as small a volume as possible. In the presence of alcohol, however, precipitation takes place rapidly, and even 0.5 mgm. of magnesium will give a distinct turbidity in this solution (containing 250 ccm. water and 50 ccm. alcohol) within half an hour, and the precipitate settles out on further standing. The presence of a small precipitate may then be detected by rotating the solution so as to cause the precipitate to collect in the centre. If calcium is present in this procedure, even as small an amount as 3 mgm. will give a distinct precipitate of calcium phosphate; it is therefore very important to precipitate the calcium completely as oxide in P. 86.

Analysis of the Alkali Group

Procedure 91. — Evaporate the filtrate from the $(NH_4)_2CO_3$ precipitate (P. 81) almost to dryness in a casserole; acidify with HCl; evaporate to dryness, and ignite the residue gently to a temperature below dull redness until no more white fumes come off, taking care to heat the sides as well as the bottom of the dish. Add about 10 ccm. water, warm, filter, evaporate the filtrate to dryness, and ignite again (to ensure complete removal of the ammonium salts). Add 5–10 ccm. water, and if necessary filter through a small filter. Test about one-third of the filtrate [first for lithium by *P. 91*a* and then] for potassium by P. 92; test the remainder of the filtrate for sodium by P. 93–94.

Notes.— 1. Great care must be taken to remove the ammonium salts completely, since the presence of even 1–2 mgm. of an ammonium salt would show the same reaction as potassium. The residue must not, however, be heated to redness, since the alkali elements might then be lost by the volatilization of their chlorides.

2. A brown or black residue of organic matter, coming from impurity in the ammonium salts used in the course of analysis and from the alcohol and filter paper, usually remains upon treating the ignited residue with water. Sometimes, owing to the presence of this organic matter, the aqueous solution after the first ignition has a dark or yellow color, but it is usually clear after the residue is heated a second time.

3. The larger portion of the solution is used for the detection of sodium, since the test for this element is less delicate than the tests for lithium and potassium.

***Procedure 91a.** — If lithium is to be tested for, evaporate one-third of the aqueous solution (P. 91) to 2 or 3 ccm. Pour it into a large test tube or small flask; add 0.3–0.5 ccm. 10% NaOH solution, and filter if there is a precipitate. Add 1–2 ccm. 10% $Na_2HPO_4.12H_2O$ solution, heat to boiling, add 1 ccm. alcohol, shake, and boil gently for about half a minute; add another portion of alcohol, and boil again for a few seconds. (White precipitate, presence of LITHIUM.) Filter, remove the filtrate, and wash the precipitate thoroughly with NH_4OH (0.96).

Dissolve the precipitate in dilute HCl, evaporate the solution to a few drops, dip the loop of a clean platinum wire into it, and introduce the loop into a colorless gas flame. (Brilliant red flame, presence of LITHIUM.)

To the filtrate from the Na_2HPO_4 precipitate add acetic acid until it is slightly acid, evaporate the solution to a few drops, and add 3–5 ccm. in water. Test the solution for potassium by P. 92.

Notes.— 1. If magnesium was not completely removed in the $(NH_4)_2CO_3$ treatment, it precipitates upon the addition of NaOH; it should be filtered off, since otherwise it would be converted into phosphate and be mistaken for lithium.

2. Li_3PO_4 is difficultly soluble in both hot and cold water; but the solubility is still less in an alkaline solution, since its hydrolysis into $(Li^+)_2HPO_4^{--}$ and Li^+OH^- is then diminished. The presence of NaOH is, moreover, necessary, in order to neutralize the acid formed in the reaction between the lithium salt and Na_2HPO_4. The tendency of Li_3PO_4 to form a supersaturated solution is overcome by heating the mixture, and by the addition of alcohol. Under the conditions of the procedure, 0.3 mgm. Li may be easily detected in the portion of solution used, and even 0.2 mgm. when the second portion of alcohol is added and the mixture again boiled.

3. The alcohol is expelled before testing the filtrate for potassium, because the presence of both alcohol and Na_2HPO_4 in a $Na_3Co(NO_2)_6$ solution causes the formation of a violet precipitate on standing. If a precipitate of Li_3PO_4 is formed by Na_2HPO_4 alone, the addition of alcohol and the subsequent evaporation are unnecessary.

4. Before making the confirmatory test, it is important to wash out the sodium salts as far as possible, otherwise the yellow color of the sodium flame may completely obscure the red color due to lithium. When the amount of lithium present is very small (0.2–0.3 mgm.),

there will always be enough sodium present to cause the flame of lithium to appear of a reddish yellow, instead of brilliant red color.

5. If a small spectroscope is available, time can often be saved by examining with it the solution before the addition of NaOH and Na_2HPO_4; for if the characteristic red line of lithium is absent, this procedure may be omitted. If present, this procedure will serve to give an estimate of its quantity, which can hardly be formed from an ordinary spectroscopic examination.

Procedure 92. — To one-third of the solution (P. 91) [or to the filtrate from the Na_2HPO_4 precipitate (*P. 91*a*)], whose volume should not exceed 5 ccm., add a few drops of acetic acid, if the solution is not already acid, and an equal volume of $Na_3Co(NO_2)_6$ reagent. If no precipitate forms at once, let the mixture stand for at least 15 minutes. Filter, and wash the precipitate thoroughly with water. (Yellow precipitate, presence of POTASSIUM.)

Dissolve the precipitate, or a portion of it, in hot dilute HCl, evaporate to a few drops, dip a clean platinum wire into the solution, and introduce it into a colorless gas flame, viewing the flame through a sufficient thickness of blue cobalt glass to cut off sodium light. (Violet flame, presence of POTASSIUM.)

Notes.— 1. To prepare the solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, used as a reagent, dissolve 100 grams $NaNO_2$ in about 200 ccm. water, add 60 ccm. 30% acetic acid and 10 grams $Co(NO_3)_2.6H_2O$; let the mixture stand for a day or two, filter off any precipitate that is formed (such as $K_2NaCo(NO_2)_6.H_2O$, arising from the presence of potassium as an impurity in the reagents), and dilute the solution to 400 ccm. For the chemical reactions involved, see Part III, P. 69, N. 1.

2. The presence of 0.3 mgm. of potassium in 5 ccm. of solution may be easily detected within 5 or 10 minutes, and an even smaller amount on long standing. The yellow color of the precipitate is best seen on the filter after washing out the $Na_3Co(NO_2)_6$ thoroughly. The solution must not be alkaline when the $Na_3Co(NO_2)_6$ reagent is added, since $Co(OH)_3$ would then be precipitated. In the presence of an ammonium salt (containing even 0.5–1.0 mgm. NH_4) a precipitate is obtained very similar in appearance to that obtained with potassium; but moderate amounts of the alkaline-earth elements or of lithium do not interfere with the test.

3. The flame test for sodium is so much more delicate than that for potassium that the yellow color due to a trace of sodium may completely

obscure the color given by a moderate amount of potassium. A sufficient thickness of cobalt blue glass is used to absorb the yellow rays completely, and thus permit the violet rays due to potassium to be seen. Comparative experiments with known solutions ought always to be made, unless the analyst is perfectly familiar with the appearance of the flames. If a spectroscope is used, the characteristic potassium line will be found near the red end of the spectrum.

Procedure 93. — In the absence of lithium (*P. 91*a*) or of much potassium (P. 92), test the remainder of the solution (P. 91) for sodium by P. 94.

If much potassium was found (and no lithium), add about 1 ccm. H_2SO_4 (1.84), evaporate in a casserole, and heat strongly until the white fumes cease to come off; let the mixture cool; add a few drops of water and 10% KOH solution until the solution is alkaline. Evaporate to about 2 ccm., cool, filter or decant off the solution, wash the crystals with a few drops of water, and test the solution for sodium by P. 94.

*If lithium is present, evaporate the solution to 2 ccm. (or 5 ccm. if much lithium is present); add 1 ccm. NH_4OH (0.90) and 2–4 ccm. 20% NH_4F solution; shake, and filter after a few minutes. To the filtrate add HCl, evaporate to dryness (in a platinum dish under a hood), heat to expel ammonium salts, add HCl, and evaporate to dryness. Dissolve in a little water, and treat the solution by P. 94, or by the preceding paragraph if much potassium is present.

Notes.—1. The presence of a large amount of potassium salt, as KCl or KNO_3, in P. 94 greatly decreases the delicacy of the test for sodium. The process here recommended for the removal of a large part of the potassium depends on the relatively slight solubility of K_2SO_4 (as compared with KCl or KNO_3), and on the fact that the saturated solution may be easily separated from the heavy crystals of K_2SO_4 either by decantation or by filtering through a small filter. In the presence of 300 mgm. potassium as chloride, 7 mgm. of sodium may escape detection if the mixture is treated directly by P. 94, but the present process enables 2–3 mgm. to be found. Unless the solution contains more than 50–100 mgm. potassium, this treatment is unnecessary.

*2. Since even 2 mgm. of lithium will interfere with the test for sodium in P. 94, the lithium must be removed before making this test. The precipitation as LiF is not complete; but, if the directions are followed, the filtrate will not contain more than 1 mgm. of lithium. The

process will not be satisfactory if the volume of the solution is too large or if too little NH_4F is used. If much sodium is present, some NaF will also be precipitated; but the filtrate will contain 50–100 mgm. of sodium if the volume is not less than 5 ccm.

*3. As an alternative process for the separation of the alkali elements, the lithium may be first precipitated as fluoride, and potassium and sodium tested for in separate portions of the filtrate. In this case, owing to the precipitation of NaF when much is present, it is always necessary to test for lithium in the NH_4F precipitate, which may be done by dissolving it in HCl, evaporating in a platinum dish, dissolving, and treating with Na_2HPO_4 by *P. 91a. When LiF is precipitated as directed in the present procedure, it is just possible to detect and confirm 1 mgm. Li. If the volume is decreased in order to obtain a more delicate test, the amount of sodium that remains in solution is also greatly decreased. This alternative process has therefore no advantages over the one adopted.

*4. When only chlorides are present, lithium may be conveniently separated from sodium (and potassium) by extracting the dry chlorides with 5–10 ccm. of a mixture of equal volumes of absolute alcohol and ether, in which LiCl alone dissolves; but the method is not applicable in all cases; for example, when sulphates are present.

Procedure 94. — If the solution that is to be tested for sodium (P. 93) reacts acid with litmus paper, add 10% KOH solution, drop by drop, until it is neutral or slightly alkaline. Evaporate the solution to about 1 ccm. and cool it. Add 1–2 ccm. $K_2H_2Sb_2O_7$ reagent; pour the mixture at once into a test tube, and let it stand for at least half an hour, or, better, over night. (White crystalline precipitate, presence of SODIUM.)

Decant off the solution, wash the precipitate several times with water, and dissolve it in a little HCl. Evaporate the solution to a few drops, and introduce a little of it on a platinum wire into a colorless gas flame. (Brilliant yellow flame, presence of SODIUM.)

Notes.— 1. The dipotassium dihydrogen pyroantimonate ($K_2H_2Sb_2O_7$) reagent is prepared as follows: Add 2 grams of the best commercial salt to 100 ccm. boiling water, boil for about 1 minute until nearly all the salt is dissolved, quickly cool the solution, add about 3 ccm. 10% KOH solution, and filter. If a (flocculent) precipitate settles out on standing, decant off the clear solution. This reagent will usually keep for several months, but it should be tested frequently with a known solution of a

pure sodium salt. When a pyroantimonate solution is made slightly acid, it decomposes rapidly with precipitation of metantimonic acid. The same reaction takes place slowly in neutral solutions, owing to hydrolysis.

2. In this test with the antimonate, if 2 ccm. of the reagent are added to 1 ccm. of solution, 2 mgm. Na should give a distinct crystalline precipitate in less than 5 minutes, 1 mgm. within 30 minutes, and a smaller amount on standing several hours. The precipitate is a heavy crystalline, granular one, and usually adheres in part to the glass, where it can best be seen by tilting the test tube. Although in a solution of a pure sodium salt 1 mgm. of sodium is easily detected, yet in an actual analysis, owing to the presence of potassium salt and of certain substances that obscure the test, it is often difficult to detect less than 2 or 3 mgm. Thus a distinct turbidity is produced by even 0.1–0.2 mgm. of calcium barium or magnesium, and by 1–2 mgm. of aluminum. These light, flocculent precipitates are, however, very different from the heavy crystalline precipitate obtained with sodium, especially if the mixture has been allowed to stand a few hours. These crystals may be separated from a flocculent precipitate by shaking the mixture, waiting long enough for the heavy crystals to settle and decanting off the suspended, flocculent precipitate.

3. In the flame test the yellow color is to be regarded as a confirmation of the presence of an appreciable amount of sodium in the sample only when a brilliant, large, spreading flame is obtained. Owing to the delicacy of the test, there is always sufficient sodium present to give a slight yellow color. The chief value of this test is in proving the absence of lithium, since the precipitate due to lithium is very similar in appearance to sodium pyroantimonate.

Test Analyses

The following analyses were made to test the efficiency of the process. Nos. 184, 185, 187, 189, 193, 195 were made by Mr. A. B. Babcock, almost all of them as unknowns.

Analyses 182–205 were begun at P. 81.

T. A. No.	182	183	184	185	186–187	188–189
Ba	500 S	500 S	500 S	500 S	500 S	500 S
Sr	0 S	1 F[1]	3 F[1]	5 S—[1]	1 S	0 S
Ca	0 S[2]	1 S	. .	. .	. .	. .
Mg	0 S	1 S	. .	. .	. .	. .

T. A. No.	190	191	192	193	194–195	196
Ba	1 S	0 S	0 S	1 S	0 S	1 S
Sr	400 S	400 S	0 S	0 F[3]	0 S	1 S
Ca	0 S[2]	1 S	500 S	500 S	0 S[2]	1 S
Mg	0 S	1 S	0 S	1 S	400 S	400 S

T. A. No.	197	198	199	200–201	202	203	204	205
Sr . . .	. .	. .	. .	. .	. .	. .	200 —	200 —
Mg . . .	400 —	400 —	400 —	5 —	5 —	5 —	. .	. .
Li . . .	0 S	1 S—[6]	1 S—[6]	. .	. .	. .	0 S	1 S
K . . .	0 S	1 F[5]	1 S—	0 S	2 S	1 S	0 S	1 S
Na . . .	0 S[4]	2 F[5]	2 D	0 S[4]	4 S	2 S[7]	0 S	2 F[5]

Analyses 206–213 were begun at *P. 91*a*. In each case the whole solution was used in making each test, instead of only one-third as directed in P. 91.

T. A. No.	206	207	208	209	210	211	212	213
Li	0 S	0 S	1 S	0.3 S[9]	0 S	0.3 S[9]	100 S	100 S
K	0 S[8]	0.5 S	0 S[8]	. .	170 S	170 —	0 S	0.5 S
Na	300 —	300 —	200 —	300 —	. .	. .	. .	. .

Analyses 214–221 were begun at P. 93. The whole solution was used in testing for sodium, instead of two-thirds as directed in P. 91.

T. A. No.	214	215	216	217	218	219	220	221
Li	. .	. .	. .	. .	. .	100 —	100 —	100 —
K	300 —	300 —	200 —	300 —	300 —	. .	. .	. .
Na	0 S	3 S	2 S[7]	2 F	1 F	0 S	2 S	1 F

NOTES

[1] In Analyses 183–185 strontium was carried down with $BaCrO_4$ in P. 82 because the K_2CrO_4 reagent was added all at once in precipitating $BaCrO_4$, instead of slowly as directed.

[2] In testing for calcium in T. A. 182, 190, 194, and 195, very small precipitates were obtained, which were estimated to contain only 0.1–0.2 mgm. Ca. The precipitates obtained in T. A. 183, 191, and 196 when 1 mgm. Ca was present were much larger.

[3] In T. A. 193 several mgm. Ca were precipitated as chromate in P. 84, probably because a little too much alcohol was added. The precipitate was filtered off and dissolved in HNO_3; 10 ccm. 30% acetic acid were added, and NH_4OH to precipitate $Cr(OH)_3$; P. 84 was repeated. Less than 0.5 mgm. Sr was found, which was present as impurity in the calcium salt. The calcium used in T. A. 192 was first freed from strontium by means of P. 84.

[4] In the tests for sodium in T. A. 197 and 200, small flocculent precipitates were obtained corresponding to 0.2–0.3 mgm. Mg. In T. A. 201 a perfect blank was obtained.

[5] The $Na_3Co(NO_2)_6$ reagent used in testing for K in T. A. 198, and the $K_2H_2Sb_2O_7$ reagent used in testing for sodium in T. A. 198 (and possibly 205), were not properly made and were not used in the other experiments.

[6] In T. A. 198 and 199 lithium was confirmed by means of a small spectroscope.

[7] The sodium tests in T. A. 203 and 216 were distinct after standing several hours.

[8] In T. A. 206 and 208 small precipitates corresponding to 0.1–0.2 mgm. K separated, owing to presence of potassium in the NaOH reagent used in *P. 91*a*.

[9] In T. A. 209 and 211 the precipitate of Li_3PO_4 did not form until the second portion of alcohol was added and the solution boiled, but the precipitate was then very distinct.

These analyses, together with the experiments on the delicacy of the separate tests, show that 1 mgm. of each element except sodium can be detected in any combination; also that 2 mgm. of sodium (in the sample) can be found in simple combinations, and 3 mgm. in every case except in the presence of a very large amount of potassium (T. A. 217).

Confirmatory Experiments and References

P. 81, N. 3-5: *Precipitation of Alkaline-Earth Elements by Ammonium Carbonate.* — For the precipitation of $MgCO_3.(NH_4)_2CO_3.4H_2O$, see Gooch and Eddy, *Am. J. Sci.* [4] **25**, 444 (1908); *Z. anorg. Chem.*, **59**, 427 (1908).

Varying small amounts of Ca, Sr, Ba and Mg as nitrates, in separate experiments, were dissolved in 4 ccm. HCl (1.12); the solutions were neutralized with NH_4OH and diluted (or evaporated) to 10 ccm.; 30 ccm. of the $(NH_4)_2CO_3$ reagent (Note 2) and finally 30 ccm. alcohol were added; the mixtures were shaken frequently and examined at intervals, with the following results:

0.5 mgm.	Ca.	Sr.	Ba.	Mg.
Solution distinctly turbid in	5	5	5–10	15–20 minutes
Very distinct test in	10	15–20	20–30	30 minutes

With 1 mgm. the same results were obtained more quickly in each case; with 2 mgm. a distinct test was obtained in less than 5 minutes in each case. Even with 0.3 mgm. Mg a better test was obtained in half an hour than in a blank experiment (with no magnesium) over night.

The above experiments were repeated with 500 mgm. of each element; the precipitates were thick and gelatinous, but soon became more crystalline when the mixtures were shaken. The precipitates were filtered off after half an hour, and the filtrates allowed to stand: no precipitate separated in any case. Each filtrate was finally evaporated almost to dryness and tested, — in the case of calcium, with NH_4OH and $(NH_4)_2C_2O_4$, strontium and barium with H_2SO_4, and magnesium with NH_4OH, Na_2HPO_4, and alcohol: no calcium was found, less than 0.1 mgm. Ba or Mg, and less than 0.2 mgm. Sr. — The experiment with 500 mgm. Mg was repeated, except that the mixture was filtered after 15 minutes: a small precipitate separated in the filtrate on standing which was estimated to contain 1 to 2 mgm. Mg.

To determine the effect of shaking, the experiment with 500 mgm. Mg was repeated, except that the mixture was shaken only once at the beginning of the experiment; the mixture was filtered after half an hour, and the filtrate allowed to stand: a precipitate separated corresponding to 2 or 3 mgm. Mg. — It was also observed in the case of each element that the precipitates became crystalline more rapidly, and were much more easily filtered off if the mixtures were shaken frequently.

To determine the effect of the addition of alcohol, the experiment with

500 mgm. Mg was repeated several times, except that 10–20 ccm. alcohol were added instead of 30 ccm.: on filtering after half an hour and allowing the filtrates to stand over night, precipitates formed corresponding to several mgm. Mg, the amounts increasing rapidly as the amount of alcohol decreased. — The experiments with 0.5–2 mgm. of each element were repeated, except that no alcohol was added: with barium the precipitates formed as quickly as in the presence of alcohol, and with strontium almost as quickly; but in the experiments with 0.5 and 1.0 mgm. Ca or Mg no precipitates were obtained.

Experiments with 0.5 and 1.0 mgm. of each element to determine the effect of dilution showed that the solutions became turbid somewhat less quickly when the volume of the solution before adding the $(NH_4)_2CO_3$ reagent was 20 ccm. instead of 10 ccm. The difference was most marked in the case of magnesium, and 0.5 mgm. might easily escape detection if the volume were still greater.

A large number of experiments similar to those described above were performed with another $(NH_4)_2CO_3$ reagent containing in 30 ccm. about 5 grams ammonium carbonate and 20 ccm. NH_4OH (0.90), *i.e.*, less $(NH_4)_2CO_3$ and more NH_4OH than the regular reagent: the results were almost identical.

The following experiments were performed to determine the effect of heating. 20 mgm. Mg as $MgCl_2$ were dissolved in 4 ccm. HCl (1.12); the solution was neutralized with NH_4OH and diluted to 10 ccm.; 30 ccm. of a solution containing 10 ccm. NH_4OH (0.90) and 3 grams $(NH_4)_2CO_3$ were added: a large precipitate appeared quickly. After several minutes the mixture was heated gently: the precipitate dissolved and a clear solution resulted at 60–70°. The mixture was cooled rapidly to room temperature: a large precipitate separated, showing that the magnesium is much more completely precipitated at low temperatures. After half an hour the precipitate was filtered off, and Na_2HPO_4 and alcohol were added to the filtrate: a precipitate separated that was estimated to contain about 4 mgm. Mg. — In separate experiments 1 and 2 mgm. of Ca, Sr, and Ba as chlorides were dissolved in HCl (1.12); the solutions were neutralized with NH_4OH (0.90) and an excess of 10 ccm. added; the solutions were diluted to 40 ccm., 3 grams powdered $(NH_4)_2CO_3$ were added; the mixtures were heated just to boiling, and filtered after 10 minutes; the amount of unprecipitated metal in the filtrate was estimated as described above: in each case distinct precipitates of the carbonates were obtained which filtered readily, and the filtrates were estimated to contain less than 0.1 mgm. Ba, 0.2 mgm. Sr, and 0.1 mgm. Ca. — These experiments were repeated except that to 10 ccm. of each solution were added 30 ccm. of a solution containing 20 ccm. NH_4OH (0.90) and 5 grams $(NH_4)_2CO_3$; no alcohol was added, and the mixtures were boiled

vigorously in flasks for 1 minute: the results were almost the same as before. — The last experiment was repeated with 500 mgm. Ca and with 500 mgm. Ba: in each case the filtrate contained not more than 0.1 mgm. of the element, and the precipitate was more granular and more readily filtered than when the carbonate was precipitated in the cold in the presence of alcohol.

1 mgm. Ba as chloride was dissolved in 4 ccm. HCl (1.12), the solution was neutralized with NH_4OH (0.96), and an excess of 4 ccm. added; after dilution to 40 ccm. 3 grams powdered $(NH_4)_2CO_3$ were added, the mixture was heated to boiling and allowed to stand: the solutions remained clear for at least half an hour. — The experiment was repeated with 2 mgm. Ba: the solution remained clear for a minute or two after boiling, and then a very small precipitate formed. On standing for a day or two, however, nearly all the barium precipitated. These results, together with those in the preceding section, show that the precipitation of barium is greatly accelerated by the presence of a large excess of NH_4OH.

1, 2, 3, and 5 mgm. Mg as $MgCl_2$ were dissolved separately in 4 ccm. HCl (1.12); the solutions were neutralized with NH_4OH and diluted to 10 ccm.; 30 ccm. of a solution containing 10 ccm. NH_4OH (0.90) and 5 grams $(NH_4)_2CO_3$ were added; the mixtures were shaken frequently. The experiments were repeated with twice as much free NH_4OH in the same volume. The results showed that precipitates formed more quickly in the solutions containing more magnesium, but that there was very little difference between the two series of experiments. — In another series of experiments with much less NH_4OH, the magnesium precipitates formed much less rapidly. — In a series of experiments with 20 ccm. NH_4OH (0.90) and 3 grams $(NH_4)_2CO_3$ the precipitation of the magnesium took place much more slowly than in the experiments with 5 grams $(NH_4)_2CO_3$, and the filtrates after 16 hours contained 0.5–1.0 mgm. Mg instead of 0.1–0.2 mgm. Therefore the most favorable conditions for the complete and rapid precipitation of magnesium are to have the solution very concentrated with respect to both NH_4OH and $(NH_4)_2CO_3$. As shown above, the addition of alcohol enables 0.5 mgm. Mg to be detected in half an hour; but this result depends also upon the presence of large amounts of NH_4OH and of $(NH_4)_2CO_3$.

P. 81, N. 6: *Precipitation of Lithium by Ammonium Carbonate.* — 150 mgm. Li as chloride were treated by P. 81 exactly as described in the first experiments under N. 3 and 4 above: after half an hour the solution was perfectly clear and there was no precipitate; after 5 hours there was a precipitate, which, however, was smaller than that obtained with 0.5 mgm. magnesium. The experiment was repeated with 200 mgm. Li: a granular precipitate separated very slowly; it was very small in 30 minutes, but after 24 hours it was estimated to contain 20–40 mgm. Li.

Behavior of Lithium in the Analysis of the Alkaline-Earth Group. —

100 mgm. Li as LiCl were dissolved in acetic acid and treated by P. 82–88: no precipitate whatever was obtained in the procedures for the detection of Ba, Sr, and Mg, and only a very small one in that for the detection of Ca, which corresponded to 0.2–0.4 mgm. Ca, and was doubtless due to the presence of calcium as an impurity.

P. 82, N. 1–3: *Solubility of Barium and Strontium Chromates in Water.* — According to the conductivity measurements of Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 241 (1893), the solubility of $BaCrO_4$ is 1.5×10^{-5} mols per liter at 18° and 2.0×10^{-5} at 25°. — Meschezerski, *Z. analyt. Chem.*, **21**, 399 (1882), found that its solubility at the boiling point of water is 1.7×10^{-4} mols per liter: also that in the precipitation of $BaCrO_4$ foreign substances are carried down with the precipitate. — R. Fresenius, *Z. analyt. Chem.*, **29**, 413–419 (1890), collected earlier data, and also showed experimentally that the solubility of $BaCrO_4$ is somewhat increased by ammonium salts and in a marked degree by acetic acid. He described a method of separating barium and strontium by precipitating $BaCrO_4$, but found that two precipitations were necessary in order to obtain the barium free from strontium.

R. Fresenius (*loc. cit.*, 419) determined the solubility of $SrCrO_4$ at 15° to be 5.9×10^{-3} mols per liter; he found that the presence of ammonium salts increased the solubility, but to a much less extent than dilute acetic acid.

The Precipitation of Barium as Chromate. — 0, 0.5, 1, and 2 mgm. Ba as nitrate were dissolved separately in 10 ccm. 30% acetic acid; the solutions were neutralized with NH_4OH, 3 ccm. acetic acid were added, and the mixtures were treated by P. 82: in the experiment with 2 mgm. the mixture became turbid at once on adding K_2CrO_4 to the hot solution; in the experiment with 1 mgm. the turbidity was less marked but was distinct; in the experiment with 0.5 mgm. the turbidity could hardly be distinguished at all, even by comparison with the solution obtained in the blank experiment. Each of the mixtures was filtered twice, and the precipitate was washed with cold water until the color of K_2CrO_4 in the filter had disappeared: the yellow residue was very distinct in the experiments with 1 and 2 mgm., and was small but distinct in the experiment with 0.5 mgm; no residue could be seen in the blank experiment. The precipitates were tested by P. 83; the green flame test was obtained in each case, but was not very brilliant in the experiment with 0.5 mgm.

The experiments with 0.5 and 1 mgm. Ba were repeated, except that the precipitates were washed with 50% alcohol: the amounts of $BaCrO_4$ left in the filter seemed to be no greater than on washing with water, and the flame tests were no better; there is, therefore, no object in using the alcohol-water mixture in washing.

500 mgm. Ba as nitrate were treated by P. 82: the large granular precipitate settled quickly, and the filtrate was clear after two filtrations. 5 ccm.

20% K_2CrO_4 solution were added to the filtrate, and the mixture was boiled for 2 or 3 minutes; no precipitate separated, showing that the precipitation of barium was complete.

500 mgm. Ba as nitrate were dissolved in 10 ccm. 30% acetic acid and treated by P. 82, except that the solution was not heated before adding K_2CrO_4, and the resulting mixture was not shaken: the large precipitate was very finely divided, did not settle quickly, filtered very slowly, and ran through the filter. The turbid filtrate was heated to boiling and boiled very gently for a minute or two: on filtering a clear solution resulted.

The Separation of Barium and Strontium. — 400 mgm. Sr as nitrate and a mixture of 400 mgm. Sr and 1 mgm. Ba as nitrates were dissolved separately in 10 ccm. 30% acetic acid, and treated by P. 82: with strontium alone a perfect blank was obtained in the K_2CrO_4 test for barium; while in the experiment with 1 mgm. Ba a distinct precipitate was obtained. In the latter case the confirmatory flame test showed the presence of a little strontium with the barium, but it was possible to distinguish the green color due to barium; the presence of barium was more easily proved by means of a small spectroscope.

To determine the effect of long-continued boiling the experiment with 400 mgm. Sr was repeated; the clear solution that resulted was boiled vigorously for 2 minutes: a granular precipitate of $SrCrO_4$ began to separate and increased somewhat on continued boiling. — The experiment was repeated with 200 mgm. Sr: no precipitate separated even on boiling for 10 minutes.

A mixture of 500 mgm. Ba and 1 mgm. Sr was dissolved in 10 ccm. 30% acetic acid and treated by P. 82; the first 2–3 ccm. K_2CrO_4 solution were added a few drops at a time, and the mixture was heated and shaken frequently; the remainder of the K_2CrO_4 solution was added quickly; the filtrate was tested for strontium by P. 84: a distinct precipitate of $SrCrO_4$ was obtained, which was estimated to contain at least 0.5 mgm. Sr. — The experiment was repeated with 500 mgm. Ba mixed with 1, 3, and 5 mgm. Sr, respectively, but the 10 ccm. portion of K_2CrO_4 solution was added all at once instead of very slowly: the $BaCrO_4$ ran through the filter in each experiment, and to obtain a clear filtrate it was necessary to filter several times through the same filter, or to boil the turbid filtrate for a minute or two. The clear filtrates were finally tested for strontium by P. 84: in each of several experiments with 1 mgm. Sr no precipitate of $SrCrO_4$ formed; in the experiments with 3 mgm. the $SrCrO_4$ precipitate was estimated to contain 0.1–0.5 mgm. Sr; and in the case of 5 mgm. the precipitate contained about 1.5 mgm. Sr. Therefore, if the K_2CrO_4 reagent is added quickly in precipitating barium, the $BaCrO_4$ precipitate runs through the filter, and as much as 3 mgm. Sr may be carried down almost completely by 500 mgm. Ba in P. 82.

Effect of Varying the Excess of Acetic Acid and of Chromate. — In each of a series of experiments 0.5 mgm. Ba as nitrate was dissolved in 10 ccm. 30% acetic acid and treated by P. 82 and 83, except that the excess of 30% acetic acid added to the neutral solution in P. 82 was varied: with 2 ccm. and 4 ccm. acetic acid the tests on the filter, after washing out the K_2CrO_4, were similar to that obtained with 3 ccm. acid, and the flame tests were distinct; with 6 ccm. acetic acid the yellow precipitate on the filter could scarcely be distinguished, but a small flame test was obtained; with a larger amount of acetic acid the tests failed. The experiments were repeated with 1 mgm. Ba: with 10 ccm. acetic acid faint tests for barium were obtained; with 15 ccm. the tests failed. — A few quantitative experiments were performed with acetic acid alone, without neutralizing with NH_4OH as in the preceding experiments: the precipitation of barium was quantitative with 2 or 3 ccm. acetic acid (*i. e.*, with the amount equivalent to the K_2CrO_4 present), but the solubility of $BaCrO_4$ increased rapidly when more acetic acid was used.

The above series of experiments with 1 mgm. Ba was repeated, except that 5 ccm. 20% K_2CrO_4 (instead of 10 ccm.) were used: distinct tests for barium were obtained when 3 ccm. acetic acid were added after neutralization, but the precipitation was not quite complete; the tests were very poor with 5 ccm. excess acetic acid, and failed with 6 ccm., showing that the precipitation is less complete and that acetic acid has a greater influence when the amount of chromate is decreased.

200 mgm. Sr as nitrate and 10 ccm. 30% acetic acid were treated by P. 82, except that only 1 ccm. acetic acid was added after neutralizing with NH_4OH: a precipitate of $SrCrO_4$ separated, corresponding to about 20 mgm. Sr. — The experiment was repeated with 400 mgm. Sr: a very large precipitate separated. 400 mgm. Sr as nitrate and 10 ccm. 30% acetic acid were treated by P. 82, except that an excess of only 2 ccm. acetic acid was added: a precipitate of $SrCrO_4$ separated which was estimated to contain about 10 mgm. Sr. — The experiments with 400 mgm. Sr were repeated with 3 and with 4 ccm. excess acetic acid: no precipitate separated in either experiment (except on boiling the solutions for a minute or two). Therefore strontium, when present alone, will precipitate in this procedure if too little acetic acid is added.

State of Chromic Acid in Solution. — See Sherrill, *J. Am. Chem. Soc.*, **29**, 1641 (1907).

P. 83, N. 1: *The Flame Test for Barium.* — Compare C. E. on P. 82. 0.5 mgm. Ba as chloride was tested by P. 83: a distinct green flame was obtained. — The experiment was repeated, the barium being first precipitated as $BaCrO_4$ in P. 82: the first flash on introducing the wire into the flame was yellow, but the green color appeared for a moment as this color died

away. — The experiment was repeated in the presence of several milligrams of chromium as $CrCl_3$ and as $Cr(NO_3)_3$: the result was the same. No green flame was obtained with chromium salts alone.

1.0 mgm. Ba was precipitated in P. 82 as chromate; the precipitate was washed and dissolved in HNO_3; the solution was evaporated to 2 or 3 drops and the yellow solution was tested by P. 83: a faint green color was seen as the yellow flame died away. Excess of HCl was then added, and the mixture evaporated to a few drops: the yellow color of the solution changed to green, owing to reduction of chromate; the flame test for barium was more distinct than in the presence of HNO_3. This experiment was repeated several times, always with the same result.

P. 84, N. 1: *Solubility of $SrCrO_4$, $CaCrO_4$, and $MgCrO_4$ in Water and in Mixtures of Alcohol and Water.* — W. Fresenius and F. Ruppert, *Z. analyt. Chem.*, **30**, 677 (1891), found the solubility of $SrCrO_4$ in 29 and 53 volume per cent. alcohol at room temperature to be 6.5×10^{-4} and 1.0×10^{-4} mols per liter. The solubility of calcium chromate in 29 and 53 volume per cent. alcohol was found to be 7.8×10^{-2} and 5.6×10^{-2} mols per liter.

Mylius and Wrachem (*cf.* Seidell, *Solubilities*, 90) prepared several different chromates, $CaCrO_4$, $CaCrO_4.\frac{1}{2}H_2O$, $CaCrO_4.H_2O$, $\alpha CaCrO_4.2H_2O$, and $\beta CaCrO_4.2H_2O$; and found their solubilities in water to increase in the order given, and to decrease with rising temperature. Since the solubility of $SrCrO_4$ increases with rising temperature, the separation of calcium and strontium will be more satisfactory at room temperature, as recommended in P. 84, than at 70°, as recommended by W. Fresenius and F. Ruppert. We have found that a precipitate sometimes separates in P. 84 when a very large amount of calcium is present, and increases in amount on standing; this indicates that the solution first obtained was supersaturated with respect to one or more of these chromates.

According to Mylius and Funk, *Ber.*, 30, 1718 (1897), the solubility of $MgCrO_4.7H_2O$ at 18° is 42.0 grams $MgCrO_4$ in 100 grams of solution (sp. gr. 1.422). Schweitzer (*cf.* Seidell, *Solubilities*, 181) found the solubility of the double salt, $MgCrO_4.K_2CrO_4.2H_2O$, to be 28.2 grams in 100 grams water at 20°, which seems to indicate that the double salt is more likely to separate in P. 84 than is $MgCrO_4.7H_2O$.

Separation of $SrCrO_4$ and $CaCrO_4$ by Means of Chromate and Alcohol. — W. Fresenius and F. Ruppert determined the difference in solubility of $SrCrO_4$ and $CaCrO_4$ in water and on adding alcohol (see preceding section), and first suggested a method based on it for use in qualitative analysis: they add K_2CrO_4 to a fairly dilute solution of the chlorides, free from HCl, heat to about 70°, and then add a quantity of alcohol equal to one-third the volume of the solution. The authors state that the precipitation of strontium is not quite complete even at the point where a moderately large amount of

calcium begins to precipitate. They did not introduce ammonium salts because the solubility of $SrCrO_4$ was then somewhat increased, and they worked at 70° because the precipitation of $SrCrO_4$ was more rapid than at room temperature.

The method of separation adopted by us is essentially the same as that described by Caron and Raquet, *Bull. soc. chim.* [3], **35**, 1061–1069 (1906). A large number of experiments were performed, however, to determine the best conditions for making the separation. The presence of ammonia and ammonium salts appears to have a greater influence on the solubility of $CaCrO_4$ than on that of $SrCrO_4$, and thus makes the separation more satisfactory than in the method of Fresenius and Ruppert.

Precipitation of $SrCrO_4$ in P. 84. — 1, 0.5, 0.3, and 0.2 mgm. Sr as nitrate were treated in separate experiments by P. 84, 10 ccm. 20% K_2CrO_4 and 10 ccm. 30% acetic acid being first added in each case: in the experiments with 1 and 0.5 mgm. the mixture became turbid at once on adding 50 ccm. alcohol to the ammoniacal solution; in the two remaining experiments the mixtures became distinctly turbid on standing several minutes. Therefore the test is a delicate one, and the precipitation must be nearly complete.

To 500 mgm. Sr as nitrate were added 10 ccm. 30% acetic acid and 10 ccm. 20% K_2CrO_4 solution (*i.e.*, an excess of about 3.7 ccm.), and the mixture was treated by the first paragraph of P. 84: a very large precipitate of $SrCrO_4$ separated. This was filtered off and the filtrate treated by the second paragraph of the procedure, 5 ccm. more K_2CrO_4 solution and 10 ccm. alcohol being added: a precipitate separated at once which was estimated to contain about 20 mgm. of strontium. The filtrate was treated again in the same way: no precipitate separated on long standing, showing that even 500 mgm. of strontium is completely precipitated in the procedure.

Solution of $SrCrO_4$ on Washing. — 5 mgm. Sr were precipitated as $SrCrO_4$ in P. 84; the precipitate was collected on a filter and washed for a long time with a mixture of equal volumes of water and alcohol. Successive portions of the wash water were tested for strontium by adding K_2CrO_4 and a little NH_4OH: the first 20 ccm. contained considerable K_2CrO_4 and very little strontium; the next 100 ccm. contained about 2.5 mgm. Sr; the next 100 ccm. contained about 1.5 mgm. Sr, and the residue on the filter was estimated to be only about 0.3 mgm. Sr. — The experiment was repeated with 1 mgm. Sr: the first 100 ccm. of wash water contained about 0.5 mgm. Sr and the second 100 ccm. about 0.4 mgm. Sr; the residue could scarcely be seen on the filter, gave only a slight flame test in P. 85, and contained less than 0.2 mgm. Sr.

Precipitation of K_2CrO_4 in P. 84. — A mixture of 10 ccm. 20% K_2CrO_4 solution and 10 ccm. 30% acetic acid were treated by P. 84, the alcohol being added slowly: 50 ccm. alcohol produced no precipitate and the solu-

tion was perfectly clear after the addition of 20 ccm. more alcohol and shaking; 5 ccm. more produced a small precipitate, and on the addition of another 5 ccm. portion, making 80 ccm. in all, the precipitate was large. It dissolved readily on washing. — The experiment was repeated, except that the alcohol (50 ccm.) was added quickly: a precipitate appeared as the alcohol was poured into the solution, but disappeared on shaking the mixture. — The experiment was repeated with 20 ccm. K_2CrO_4 solution instead of 10 ccm.: a permanent precipitate of K_2CrO_4 formed with 40 ccm. alcohol, but not with 35 ccm.

Behavior of Calcium and Magnesium towards Potassium Chromate. — 500 mgm. Ca as pure $Ca(NO_3)_2$, 10 ccm. 20% K_2CrO_4 solution, and 10 ccm. 30% acetic acid were treated by P. 84, 50 ccm. alcohol being added: no precipitate separated in half an hour, and only an insignificant one on standing over night. After pouring through a filter, 5 ccm. more K_2CrO_4 solution and 10 ccm. alcohol were added: a precipitate separated slowly, which after standing several hours corresponded to only several milligrams of calcium. — The experiment was repeated, except that after the addition of the extra K_2CrO_4 and alcohol the mixture was allowed to stand several days: the precipitate separated slowly as before, but was large after several days.

400 mgm. Mg as nitrate, 10 ccm. 20% K_2CrO_4 solution, and 10 ccm. 30% acetic acid were treated by P. 84: the solution remained clear on adding 50 ccm. alcohol, but a very small crystalline precipitate separated out on standing several hours, which was very different in appearance from $SrCrO_4$.

P. 85, N. 1–2: *Action of a Mixture of Sodium Oxalate and Carbonate on Calcium and Strontium Solutions.* — In a series of experiments 5 mgm. Ca as nitrate were added to varying amounts of a 10% Na_2CO_3 solution; 30 ccm. 3% $Na_2C_2O_4$ solution were added, and the mixture boiled for 5 minutes. The precipitate was filtered off, washed well, and a 5 ccm. portion of dilute acetic acid was poured three times through the filter; the residue was dissolved in dilute HCl. The amount of calcium in each solution was estimated by adding NH_4OH and $(NH_4)_2C_2O_4$ and boiling. The results are given in the following table:

Amount of 10% Na_2CO_3 used	2.0	4.0	5	6 ccm.
Amount of calcium in HAc	0.05–0.2	<0.1	1	4.5–5.0 mgm.
Amount of calcium in HCl	4.9	5.0	4	0.0–0.5 mgm.

$CaC_2O_4.H_2O$ was found to be practically insoluble in cold dilute acetic acid; therefore these results show the amounts of calcium present as carbonate and oxalate, respectively. The test with $(NH_4)_2C_2O_4$ enabled 0.05 mgm. Ca to be detected.

Similar experiments were tried with 5 mgm. Sr; 30 ccm. 3% $(Na)_2C_2O_4$ were first added and then in separate experiments 1 ccm. and 2 ccm. 10% Na_2CO_3: in such case all the strontium dissolved in the acetic acid, showing that the strontium oxalate was converted into carbonate in this treatment. SrC_2O_4 was found to be nearly insoluble in acetic acid, and the test with $(NH_4)_2C_2O_4$ scarcely enabled 0.5 mgm. Sr to be detected.

Effect of the Presence of Barium Chromate. — To 5 mgm. Ba as nitrate were added in succession 20 mgm. K_2CrO_4 dissolved in a little water, 30 ccm. 3% $Na_2C_2O_4$, and 2 ccm. 10% Na_2CO_3; the mixture was boiled for 5 minutes and filtered, and the precipitate washed: the precipitate was yellow, showing the presence of some $BaCrO_4$. 5 ccm. dilute acetic acid was poured through the filter, K_2CrO_4 was added, and the mixture boiled: a precipitate corresponding to about 3 mgm. Ba resulted. — The experiment was repeated with 50 and with 100 mgm. K_2CrO_4: not more than 0.5 mgm. Ba dissolved in the acetic acid, showing that in these experiments $BaCrO_4$ was not converted into carbonate, as in the preceding experiment with less K_2CrO_4.

P. 85, N. 3: *Delicacy of Test for Strontium.* — 0.5 and 1.0 mgm. Sr as nitrate were treated by P. 85: satisfactory tests were obtained in each case. — The experiments were repeated, except that the strontium was first precipitated as chromate by P. 84: the results were the same. — In an experiment with no strontium a perfect blank test was obtained. The test with ammonium carbonate enables 0.3 mgm. Sr in the acetic acid solution to be easily detected.

Effect of the Presence of Calcium and Magnesium. — 5 mgm. Ca as nitrate were treated by P. 85, the mixture being boiled for 5 minutes: a perfect blank was obtained. — The experiment was repeated with 10 mgm., the mixture being boiled 5 minutes: the result was the same. — The experiment was repeated three times with 30 mgm. and once with 50 mgm. Ca: in two of these experiments good blank tests were obtained, but in the third and in the experiment with 50 mgm. a small turbidity resulted, corresponding to about 0.3–0.4 mgm. Ca. — No test was obtained with $(NH_4)_2CO_3$ when the acetic acid solution contained 0.2 mgm. Ca. The results obtained above, when calcium was tested for in the acetic acid solution with $(NH_4)_2C_2O_4$, show that this solution always contained 0.05–0.2 mgm. Ca.

50 mgm. Mg as nitrate were treated by P. 85: a small gelatinous precipitate of $Mg(OH)_2$, corresponding to 5–10 mgm. Mg, was obtained, which dissolved in the acetic acid; no precipitate formed in the ammonium carbonate solution in several hours, but a small crystalline one separated out over night.

P. 86, N. 1: *Solubility of $CaC_2O_4.H_2O$ in Water.* — See A. F. Holleman, *Z. physik. Chem.*, **12**, 129 (1893); Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 241 (1893); Richards, McCaffrey, and Bisbee, *Z. anorg. Chem.*, **28**, 85

(1901). According to the last-named authors the solubility is 4.7×10^{-5}, 6.5×10^{-5}, and 9.6×10^{-5} mols per liter at 25°, 50°, and 95°, respectively.

Solubility of $MgC_2O_4.2H_2O$. — According to the conductivity measurements of Kohlrausch, *Z. physik. Chem.*, **50**, 356 (1905), the solubility at 18° is 2.6×10^{-3} mols per liter.

Precipitation of Calcium by Ammonium Oxalate. — 0, 0.3, 0.5, 1.0, and 2 mgm. Ca as nitrate were dissolved separately in 10 ccm. 15% acetic acid, and the solutions were treated by P. 84 and 86, 25 ccm. 4% $(NH_4)_2C_2O_4.H_2O$ solution being added in each case to the hot solution in P. 86: in the experiments with 1 and 2 mgm. the mixtures became slightly turbid at once and the suspended precipitates were very easily seen in a minute or two; with 0.5 mgm. the solution was at first almost clear, but the precipitate could be easily seen after 5 minutes; with 0.3 mgm. a very small precipitate settled out in about an hour; with the solution containing no calcium a good blank test was obtained. In the experiment with 0.5 mgm. the mixture was filtered after about 20 minutes, and the precipitate was tested by P. 87: a small precipitate of $CaSO_4$ separated quickly on adding alcohol to the H_2SO_4 solution.

The experiments with 1 and 2 mgm. Ca were repeated, except that the ammonium oxalate was added to the cold solution: no precipitates separated in the cold, but the solutions became turbid on heating to boiling. The mixtures were shaken and allowed to stand several minutes: the precipitates did not run through the filter. In experiments in which a large amount of calcium was precipitated in the cold filtration was slow, and the precipitate ran through the filter.

Separation of Calcium from Magnesium by Ammonium Oxalate. — 400 mgm. Mg as chloride were dissolved in 10 ccm. 30% acetic acid; the solution was neutralized with NH_4OH (0.90) and an excess of 3 ccm. added; the mixture was diluted to 250 ccm.; 10 ccm. 20% K_2CrO_4 solution and 50 ccm. alcohol were added, making the total volume 310 ccm.; the mixture was heated to boiling and 20 ccm. 4% $(NH_4)_2C_2O_4.H_2O$ solution added: a small precipitate corresponding to about 0.5 mgm. Ca formed. This was filtered off, 15 ccm. more oxalate solution were added, and the mixture was boiled: no more precipitate separated. — The experiment was repeated, except that 1 mgm. Ca as nitrate was also added: a larger precipitate separated than in the former case. This was filtered off and treated by P. 87: a precipitate of $CaSO_4$ separated at once on adding alcohol.

The experiment with 400 mgm. Mg was repeated, except that the total volume of the solution was 210 instead of 310 ccm.: a large precipitate separated on cooling. — This experiment was repeated with 300 mgm. Mg, the total volume being 210 ccm.: the hot solution was clear after adding the ammonium oxalate, but a small precipitate separated on cooling; this pre-

cipitate dissolved when the mixture was heated to about 70°, but separated again on cooling, thus showing that the solubility of the magnesium precipitate increases rapidly with the temperature. — The experiment was repeated with 200 mgm. Mg, the volume being 200 ccm.: no precipitate separated even on long standing at room temperature. These experiments show that the volume should not be less than 300 ccm. when much magnesium is present, but that the volume may be much smaller if the amount of magnesium is small.

P. 87, N. 1: *Solubility of* $CaSO_4.2H_2O$. — For the solubility in water at temperatures between 0° and 100° see Hulett and Allen, *J. Am. Chem. Soc.*, **24**, 674 (1902). For the solubility in H_2SO_4 solutions see Cameron and Breazeale, *J. Physic. Chem.*, 7, 574 (1903). The solubility in water in mols per liter at 25° is 0.0153, and there is a maximum solubility of 0.0208 mols per liter in an acid containing 75 grams H_2SO_4 per liter. With rising temperature the solubility in H_2SO_4 increases and the maximum solubility is in more concentrated solutions. The laboratory acid of sp. gr. 1.2 contains 328 grams H_2SO_4 per liter, and the solubility of $CaSO_4$ in it is over half the maximum solubility.

Precipitation of Calcium as $CaSO_4.2H_2O$. — 0, 0.2, 0.3, 0.5, and 1.0 mgm. Ca as nitrate were dissolved in separate experiments in 5 ccm. dilute H_2SO_4 (1 volume 1.20 acid and 3 volumes water), 10 ccm. 95% alcohol were added, and each mixture was shaken: in the experiment with 1 mgm. the solution became turbid at once and a large, flocculent precipitate separated in a minute or two; with 0.5 mgm. the turbidity was distinct in 1 minute, and the precipitate appeared flocculent in 2 or 3 minutes; with 0.2 and 0.3 mgm. the solutions became slightly turbid in 5 minutes, the test was distinct in 10 minutes, and the precipitate appeared flocculent in half an hour; in the blank experiment the solution remained clear. — The experiments were repeated with H_2SO_4 (1.20): the results were the same, except that the calcium precipitated somewhat less rapidly. — Some experiments were performed with more concentrated H_2SO_4, but the results became less and less satisfactory with increasing concentration of H_2SO_4.

P. 87, N. 2: *Behavior of Strontium or Magnesium in the Confirmatory Test for Calcium.* — 10 mgm. Sr as nitrate were precipitated as oxalate by adding NH_4OH, $(NH_4)_2C_2O_4$ and heating; the mixture was filtered and the precipitate washed twice with water. A 5 ccm. portion of H_2SO_4 (1.20) was poured repeatedly through the filter, and finally 15 ccm. 95% alcohol were added to the solution: the mixtures became turbid at once; after settling the precipitates corresponded in amount to that obtained with 0 2–0.3 mgm. Ca. — The experiment was repeated with 2 mgm. Sr as nitrate, which was added directly to 5 ccm. H_2SO_4, various concentrations of H_2SO_4 being used, from 1 volume H_2SO_4 (1.20) in 10 ccm. to H_2SO_4 (1.20): in each case the result was nearly the same as before.

50 mgm. Mg as $MgCl_2$ were dissolved in 5 ccm. H_2SO_4 (1.05) and 15 ccm. alcohol were added: no precipitate separated, even on long standing.

P. 88, N. 1: *The Precipitation of Magnesium by Phosphate.* — In each of a series of experiments 0.5 mgm. Mg as $Mg(NO_3)_2$ was dissolved in 10 ccm. 30% acetic acid, 10 ccm. 20% K_2CrO_4 solution were added, the solution was neutralized with NH_4OH and diluted to 250 ccm.; 50 ccm. alcohol and varying amounts of NH_4OH (0.90) and of 7% $Na_2HPO_4.12H_2O$ solution were added and the mixture shaken. The following table shows the time in which the solution became turbid.

Excess NH_4OH (0.90).	No. Cubic Centimeters 7% $Na_2HPO_4.12H_2O$ Added.		
	10	20	30
3 ccm.	15 minutes	15 minutes	15 minutes
13 ccm.	7 minutes	3 minutes	3 minutes
30 ccm.	. .	2 minutes	2 minutes

In each case the turbidity became more distinct in a few minutes, and a crystalline precipitate settled out in 1–1½ hours. These experiments show that the presence of a considerable excess of NH_4OH makes the precipitation more rapid.

The experiment with 13 ccm. excess NH_4OH (0.90) and 2.0 ccm. 7% $Na_2HPO_4.12H_2O$ was repeated with 0.3, 0.2, 0.1, and 0.0 mgm. Mg, respectively: in the experiment with 0.3 mgm. the solution became turbid in 10 minutes, the test was very distinct in 15 minutes, and a crystalline precipitate collected within 1½ hours; with 0.2 mgm. a slight turbidity appeared in 15 minutes, the test was fairly distinct in 30 minutes, and a small precipitate had collected within 1½ hours; with 0.1 mgm. no turbidity could be seen, but a minute precipitate separated in 2 hours; in the blank experiment there was no turbidity, ahd no precipitate separated in several hours.

Precipitation of Calcium as Phosphate. — The last experiment was repeated with 2 and with 5 mgm. Ca as nitrate: in the experiment with 5 mgm. the solution became turbid almost at once, and with 2 mgm., slightly turbid, after standing about 1 hour.

***P. 91a, N. 2:** *Precipitation of Lithium as Phosphate.* — To determine the delicacy of the test, 0.3 and 0.5 mgm. Li as LiCl were dissolved separately in 3 ccm. water; 0.5 ccm. 10% NaOH solution and 1 ccm. 10% $Na_2HPO_4.12H_2O$ solution were added; the mixture was heated to boiling in a large test tube, 1 ccm. alcohol was added, and the mixture boiled: a

white precipitate formed almost at once. — The experiment was repeated with 0.2 mgm. Li: even after boiling off a large part of the alcohol the solution was almost clear, but on adding a second portion of alcohol and again boiling a very distinct precipitate was obtained. — A blank experiment was made without adding any lithium: a clear solution was obtained even after adding alcohol and boiling it off four times. — The precipitates obtained in these experiments were filtered off, washed thoroughly with cold NH_4OH (0.96), and dissolved in dilute HCl; the solutions were evaporated to about 1 ccm., and the color imparted to the flame was tried: the red color was easily seen in the experiment with 0.5 mgm. Li, but was not very distinct in that with 0.3 mgm. Li, owing to the yellow sodium flame. By means of a spectroscope, however, lithium was easily detected in both cases.

To determine the effect of the presence of alcohol, the experiment was repeated with 1 and with 2 mgm. Li, except that no alcohol was added; the test tube was heated to boiling and then placed in a steam bath near 100°: with 2 mgm. a precipitate appeared on heating, but with 1 mgm. none appeared in 10 minutes.

Experiments with varying amounts of NaOH and Na_2HPO_4 indicated that the test was most delicate when an excess of 0.3–0.5 ccm. of the 10% NaOH solution and from 1–2 ccm. 10% $Na_2HPO_4.12H_2O$ solution were used.

P. 92, N. 1–2: *Test for Potassium with Sodium Cobaltinitrite.* — For the composition of the precipitate $K_2NaCo(NO_2)_6H_2O$ see Adie and Wood, *J. Chem. Soc.*, 77, 1076 (1900); Drushel, *Am. J. Sci.* [4], 24, 433 (1907); 26, 329 (1908).

0.3 and 0.5 mgm. K as KCl were dissolved separately in 5 ccm. water and 5 ccm. of $Na_3Co(NO_2)_6$ reagent (2 days old) added: the solution became turbid within 1–4 minutes, and precipitates settled out quickly. These were filtered off and washed with water: the yellow precipitate were easily seen on the white filter. — The experiment was repeated with 0.2 mgm. K: in 20–30 minutes the solution was slightly turbid, and the precipitate began to settle out in about 2 hours. The experiment was repeated with 0.1 mgm. K: after 2 hours the solution was clear, but a small precipitate settled out in 6–10 hours. — A blank experiment was made without adding any potassium: the solution remained clear for 2 days.

To determine the effect of the age of the reagent, the experiments with 0.3 and 0.5 mgm. K were repeated, except that an old reagent was used, which had been kept in a stoppered bottle for 4 months: the results were the same.

To determine the effect of the presence of acetic acid, separate 0.5 mgm. portions of K as KCl were dissolved in 5 ccm. of solution containing, respectively, 0, 0.5, 1.0, and 2.5 ccm. 30% acetic acid, and 5 ccm. of the reagent added: in each case the solution became distinctly turbid within 1 minute. —

The experiments were repeated with 0.3 mgm. K: each solution became turbid in less than 5 minutes. Therefore the presence of acetic acid does not decrease the delicacy of the test.

Behavior of $Na_3Co(NO_2)_6$ towards Various Substances. — 2 mgm. NH_4 as NH_4NO_3 were dissolved in 5 ccm. water and 5 ccm. reagent added: the solution became turbid almost at once. — The experiment was repeated with 0.5 and 1 mgm. NH_4: with 1 mgm. the solution became turbid in about 10 minutes; with 0.5 mgm. in several hours. The turbid solutions were almost identical with those obtained when potassium was present, but the precipitate, when filtered off and washed, was found to be more orange in color than the potassium precipitate.

50 mgm. Li as LiCl were dissolved in 5 ccm. water and 5 ccm. reagent added: in 2 days only a minute precipitate settled out, corresponding to about 0.2 mgm. K. — The experiment was repeated with 100 mgm. Li: only a very small precipitate settled out on standing, which was not greater than that expected from the potassium impurity.

50 mgm. of Ca, Sr, Ba, and Mg as nitrate were dissolved in separate experiments in 5 ccm. water and 5 ccm. reagent added: no precipitate formed in 2 hours in any case.

To 5 ccm. of solution containing 1 ccm. 10% NaOH were added 5 ccm. of the reagent: the solution slowly darkened and very finely divided, was almost black in 2 minutes, and when filtered yielded a black precipitate and filtrate.

To 2 ccm. 10% $Na_2HPO_4.12H_2O$ solution were added 3 ccm. water and 5 ccm. $Na_3Co(NO_2)_6$ reagent: no precipitate formed.

To 1 ccm. alcohol and 4 ccm. water were added 5 ccm. reagent: no precipitate formed in 18 hours.

2 ccm. 10% $Na_2HPO_4.12H_2O$ solution, 1 ccm. alcohol, and 2 ccm. water were mixed and treated with 5 ccm. $Na_3Co(NO_2)_6$ reagent and the mixture allowed to stand over night: a film covered the glass and some crystals adhered to it. On filtering and washing, the film was found to be light violet and the crystals somewhat darker; on dissolving in HCl both were found to contain cobalt. — The experiment was repeated, except that the mixture was evaporated almost to dryness, to expel the alcohol, and then dissolved in 5 ccm. water before adding the $Na_3Co(NO_2)_6$ reagent: there was practically no precipitate, even on long standing.

P. 93, N. 1: *Effect of the Presence of Potassium Salts on the Test for Sodium.* — Neutral solutions of various mixtures of potassium and sodium, both as chlorides and nitrates, were evaporated in small flasks to about 1 ccm., and cooled. In each case 2 ccm. of the $K_2H_2Sb_2O_7$ reagent (P. 94, N. 1) were added; the mixture was shaken to dissolve any KCl or KNO_3 that had separated on cooling, and allowed to stand for several hours. The

following table shows the number of milligrams of sodium present in each experiment.

	Chlorides.			Nitrates.		
Test for Na.	In 10 minutes.	Over night.	Failed.	In 10 minutes.	Over night.	Failed.
300 mgm. K . . .	10	7	6	. .	6	4
200 mgm. K . . .	5	4	3	. .	3	. .
100 mgm. K . . .	3	2	1	. .	2	1
50 mgm. K . . .	2	2	1	. .	. .	. .
0 mgm. K . . .	1	. .	. .	1	. .	. .

It is evident that the presence of KCl and of KNO_3 greatly decreases the delicacy of the test for sodium.

The experiments with 300 mgm. K were repeated, except that a large part of the K was separated as K_2SO_4 by the process described in P. 93: with 3 mgm. Na a very satisfactory test was obtained in 15 minutes; with 2 mgm. Na a few small crystals separated on standing over night, but the test was practically a failure. In another experiment with 200 mgm. K and 2 mgm. Na a distinct test for sodium was obtained in about 2 hours.

P. 93, N. 2: *Action of Potassium Pyroantimonate on Lithium.* — In separate experiments 2, 5, and 10 mgm. Li as LiCl were treated by P. 94: in each experiment a crystalline precipitate very similar in appearance to $Na_2H_2Sb_2O_7.6H_2O$ separated — with 10 mgm. in a few minutes, with 5 mgm. in about 1 hour, and with 2 mgm. in 10 hours. The experiment was repeated with 1 mgm. Li: no precipitate separated in 24 hours, and only a very small one in 3 days. — The experiments were repeated with freshly prepared $K_2H_2Sb_2O_7$ reagent, to which no KOH had been added: the results were the same.

P. 93, N. 2–3: *Precipitation of Lithium and Sodium as Fluorides.* — 1 mgm. Li as LiCl was dissolved in 2 ccm. water, 1 ccm. NH_4OH (0.90) and 2 ccm. 20% NH_4F solution were added; a small precipitate separated in a minute or two, and was proved to be lithium by the flame test and by converting it into Li_3PO_4 by *P. 91*a*. — The experiment was repeated with 1 and with 2 mgm. Li except that the initial volume was 5 ccm. instead of 2 ccm.: a very distinct precipitate of LiF separated at once with 2 mgm., but the precipitate with 1 mgm. after an hour was so small that the test with Na_2HPO_4 failed.

The above experiments were repeated with 100 mgm. Na as NaCl: in the smaller volume a precipitate of NaF formed at once; in the larger volume no precipitate separated.

Experiments with 0.5 mgm. Li showed that this amount could be detected by evaporating the solution to 0.5 ccm., adding 0.5 ccm. NH_4OH (0.90) and 1 ccm. 20% NH_4F solution, but that 0.5 ccm. was then about the limit of detectability. Under these conditions a precipitate of NaF was obtained at once with 30 mgm. Na as NaCl, but not with 20 mgm.

For the precipitation of lithium as fluoride and the detection of sodium in the filtrate see T. A. 219–221.

P. 93, N. 4: *Separation of Sodium and Lithium by Alcohol Ether.* — Mixtures of chlorides of sodium and lithium were treated by the process described in the note. The lithium was confirmed by *P. 91*a*; the sodium by P. 94, including the flame test. The results are recorded as in the Test Analyses.

No.	1	2	3	4	5	6
Na	200 S	200 —	200 —	0 S	2 S	1 S—
Li	0 S	1 S	0.5 S—	100 —	100 —	100 —

In making the flame test for sodium in No. 6, the yellow flame had a reddish tinge and the spectroscope showed the presence of lithium; on standing about 24 hours a few small crystals separated in the test for sodium in No. 4, but the flame was red, not yellow. In these analyses the lithium had not been carefully washed out of the filter paper.

P. 94, N. 1–2: *Composition of Alkali Antimonates.* — Several different solid antimonates of each element are known, and formulæ have been assigned chiefly from their behavior when heated. Thus the ordinary compounds of sodium, which has the composition $NaSbO_3.3\frac{1}{2}H_2O$, loses water when heated, but the last half molecule remains even at 350° — Knorre and Olschewsky, *Ber.*, **18**, 2360 (1885). The three molecules that are given off readily are considered to be water of crystallization, and the remainder to be chemically combined; the formula is therefore written $Na_2H_2Sb_2O_7.6H_2O$. The question of the composition of the solutions is still an open one.

Test for Sodium with Potassium Antimonate. — 1 mgm. Na as NaCl was dissolved in 1 ccm. water and 2 ccm. of the freshly prepared alkaline potassium antimonate reagent (see N. 1) were added: after 5 minutes a small, nearly colorless precipitate adhering to the glass could be seen, which in 15 minutes had become much more distinct and in 30 minutes had become white and opaque. As it adhered very firmly to the glass the solution was

poured out; the precipitate was washed with water several times, and finally the test tube was filled with water: after several hours the precipitate still remained on the glass. The water was poured out and HCl added: the precipitate dissolved, more rapidly on warming. — The experiment was repeated several times with 0.5 mgm. Na: in 30–60 minutes small, colorless crystals were seen adhering to the glass, which became more distinct on standing 30–60 minutes longer, though the precipitate remained nearly colorless.

To determine the effect of the amount of antimonate used, the foregoing experiments were repeated, using different reagents, in which 1, 2, 3, 5, and 8 grams pyroantimonate were added to 100 ccm. boiling water, after which the solutions boiled for a minute or two until almost all the salt disappeared. The results are given in the following table. In each case the sodium chloride was dissolved in 1 ccm. and 2 ccm. of a reagent were added.

Pyroantimonate in 100 ccm.		1 gram.	2 grams.	3 grams.	5 grams.	8 grams.
2.0 mgm. Na	slight test in . .	5	2–5	3	10	10 minutes
	distinct test in .	5–30	5–30	5	15	30 minutes
1.0 mgm. Na	slight test in . .	7–10	5	5	20	10–60 min.
	distinct test in .	30–60	10–30	10–30	60	Over night
0.5 mgm. Na	slight test in . .	. .	30–60	30–60	No test in 1 hour	. .
	distinct test in .	90 minutes	60–90	60–90		. .

It is evident that the second and third reagents give the most satisfactory results. The former is the one recommended in the process.

Effect of the Alkalinity of the Potassium Pyroantimonate Reagent. — A solution was prepared from 2 grams of the commercial salt and 100 ccm. water as described in N. 1, but no KOH was added: it was clear and reacted neutral to litmus paper. To a portion a few drops of HCl were added: a white, flocculent precipitate separated quickly. — The neutral (2%) solution was placed in a corked test tube and allowed to stand: it remained clear over night, but after a few days a white, flocculent precipitate separated out. The clear solution was poured off and again allowed to stand: a precipitate again formed, which ran through the filter. After 6 weeks 2 ccm. of the solution were added to 1 ccm. of a NaCl solution containing 2 mgm. Na: no crystalline precipitate formed, even on standing several hours. The solution now reacted alkaline to litmus paper.— Various other strengths of the

reagent were tested in the same way, portions of the solutions being set aside before KOH was added: the 1% solution was neutral and decomposed very slowly; the 3% solution showed a very slight alkaline reaction and decomposed more rapidly than the 2% solution; the 5 and 8% solutions were distinctly alkaline, became very turbid over night, and large precipitates separated on standing.

To try the effect of the presence of KOH, a solution of the antimonate reagent was prepared by dissolving 2–3 grams of the salt in 100 ccm. boiling water and cooling; and to three 20 ccm. portions of the neutral solution were added, respectively, 0.5, 1.0, and 2.0 ccm. 10% KOH solution. These solutions were placed in corked test tubes and set aside: a flocculent precipitate separated slowly in each solution, but it was much smaller than that obtained in a corresponding solution to which no KOH had been added. After 6 weeks 2 ccm. of each solution were added to 1 ccm. portions NaCl solution containing 1 or 2 mgm. Na: a small but distinct crystalline precipitate separated in each case,—within 10 minutes with 1 mgm. Na, and within 3–5 minutes with 2 mgm.; the tests became more distinct on standing. The clear reagents were allowed to stand 3 months longer: a very small, flocculent precipitate separated in each case. The tests with 1 and 2 mgm. Na were then repeated: the results were exactly the same. A comparison of these results with those obtained above with freshly prepared solutions shows that an alkaline reagent, unlike a neutral reagent, does not deteriorate appreciably in over 4 months.

The tests with 1 and 2 mgm. Na were repeated with a freshly prepared reagent to which no KOH had been added: the results were almost exactly the same, showing that the delicacy of the test is not affected by the presence of alkali, nor by its amount.

About 3 grams of antimonate were added to 100 ccm. 0.3 to 0.5% solution of KOH, the mixture was heated to boiling, shaken well while hot, cooled, and filtered. 2 ccm. of this reagent were added to 1 ccm. NaCl solution containing 3 mgm. Na: no precipitate separated in a day, showing that the KOH must not be added to the solution until after it is cooled.

Behavior of Potassium Antimonate Reagent towards Various Substances.— In the following experiments the substance was dissolved in 1 ccm. water and 1 to 2 ccm. of the antimonate reagent added.

With 5 mgm. NH_4 as NH_4NO_3, in slightly alkaline solution, a small, flocculent precipitate separated on standing an hour or two, but did not increase on longer standing.

With 1 mgm. Ca as nitrate a large, white, gelatinous precipitate formed at once; with 0.2 mgm. Ca, marked turbidity at once; with 0.1 mgm. Ca, slight turbidity at once.

With 0.2 mgm. Ba as nitrate a slight turbidity appeared at once; with

0.1 mgm. Mg as nitrate, a slight turbidity at once; with 0.3 mgm. Mg there was a marked turbidity.

In a number of experiments 400 mgm. Mg as nitrate were precipitated as magnesium ammonium carbonate by P. 81, and the neutral filtrate tested for Na by P. 93: in one or two cases a perfect blank was obtained, but in others a small, flocculent precipitate separated corresponding to 0.1–0.3 mgm. Mg. But this turbidity was probably not due to magnesium, since in another experiment no precipitate separated when KOH was added to the filtrate; and yet a small, flocculent precipitate was obtained on adding the antimonate.

A few drops of alcohol were added to 1 ccm. of reagent: a large, white precipitate separated at once.

THE RÔLE OF VISCOSITY IN AIR SUPPORT OF A MOVING AËROPLANE

By FRANK W. VERY

LANGLEY, in his "Experiments in Aërodynamics," says (page 105), in summing up the results of his work, "that the pressure [on a moving aëroplane] is normal to the inclined surface, and hence that the effects of skin-friction, viscosity, and the like are negligible in such experiments." This involves a mistake. Viscosity, instead of being negligible, is the principal factor in the supporting power of aëroplanes at low angles. In making this criticism I wish to add that, so far as I know, this is the only serious mistake in the whole book, and it is one of interpretation, but not an error in the data of experiment. It should be noted that the statement that the pressure is normal to the inclined surface is an inference, since the observations did not have the minute precision necessary to establish this point beyond a doubt. Other considerations permit us to overturn this inference and to state that the direction of pressure differs slightly from the normal at low inclinations.

In the lateral movement of an inclined plane the stream lines enclose a partial vacuum behind the advancing edge, but the lifting power of the vacuum is small compared with the sustaining effect due to the inertia of the air. Thus in some experiments which I tried while working with Professor Langley I found that when a plane has its front edge inclined downward in the direction of advance by 7°, in which case the vacuum due to the stream lines is on the lower side of the plane, the time of fall when the plane was moving forward at velocities near 10 meters per second was still slightly greater than when the fall was from a position of rest, indicating that the downward pull of the vacuum produced by motion was not equal to the support obtained through viscosity. If the vacuum effect is incapable of overcoming viscosity in a solid plane, still less can there be any great amount of suction in the case of a bird's wing, which is an open-work structure permeable to air. Consequently the explanation of the soaring bird

as an instance of support of weight by a vacuum, which has been proposed by some theorists, will not work.

To Langley more than to any one is due the credit for demonstrating the part which the inertia of the air plays in supporting a bird. Not that he was the first to put forth this explanation, although one might suppose this to be the case from some passages in his paper on "The Internal Work of the Wind," nor is he always correct in all of the details. Thus in this paper he attributes a selecting power to the bird, which, by rotating the plane of its wings about a vertical axis, can accumulate energy from variations of the wind. He says: "The rotation of the body about a vertical axis, so as to change the aspect of the inclination, may be illustrated by the well-known habit of many soaring birds of moving in small closed curves or spirals; but it may also be observed, in view of the fact that even in intervals of relative calm, during which the body descends, there is always some wind, that in making the descents if the body, animate or inanimate, maintain its direct advance, this wind tends to strike on the upper side of the plane or pinion. Mr. G. E. Curtis offers the suggestion that the soaring bird avoids such a position when possible, and therefore turns at right angles to or with the wind, and that this may be an additional reason for his well-known habit of moving in spirals." The case is quite different here from that of vertical circling. The latter, or circling in a vertical plane, as explained by Basté, does appear to have an element of choice on the part of the bird. Not so the horizontal circling; for, as the bird rotates at a uniform rate of turning while the fluctuations of the wind are not uniform, the two variations will seldom coincide. The horizontal circling is solely to produce alternations in the relative velocity, which can be done even if the wind remains steady.

If a bird wishes to hover over a given spot on the earth's surface, it must receive the wind on the back in the alternate positions and move alternately faster and slower than the wind. It cannot ascend progressively under these circumstances, but can only balance up and down through a small range. If, however, the bird moves on in the same direction as the wind, its velocity need never fall below that of the wind. The fact that a bird can mount indefinitely by circling in a wind which exceeds a certain speed, determined by the form of the bird, proves that energy can be stored up in this way. This reserve power can only be derived from the wind. Momentum is transferred

from the moving air to the heavier body through the intermediation of the viscosity of the air, augmented in this case by the intimate hold which the multitudinous capillary surfaces of the plumage affords. If the bird chooses to expend only a part of its reserve, the animal may always preserve an actual velocity greater than that of the wind, though this does not mean that it will progress as fast in respect to a rectilinear course.

Babinet thought that he had demonstrated that a bird weighing 1 kilogram, for example, must perform continuously a work of 4.9 kilogram-meters per second in order to support itself in the air. He reasoned thus: "Gravity, acting on the bird, will make it fall 4.9 meters in the first second. It is necessary then that the bird, in order to fly horizontally, shall expend each second the work needed to raise its own weight through 4.9 meters." André, Mayor, and d'Esterno showed the fallacy of this. They say: "If instead of one second Babinet had taken two seconds for his unit of time, he would have found that the bird, falling in this time $4.9 \times 2^2 = 19.6$ meters, must raise its own weight 19.6 meters in two seconds, or 9.8 meters in one second. This work is twice as great as that which the calculation based on the second as the unit of time would give. Thus d'Esterno concluded it was necessary to assign the true value to the time during which the bird is submitted to the accelerating force of gravity. Choosing for a type a bird which gives five wing-beats per second, he estimates that each of the falls, being only able to last a fifth of a second, will be reduced to 0.2 meter. The work which will compensate the effect of these falls during an entire second will consist only in raising the bird five times each second through 0.2 meter, or to a height of 1 meter." These opinions are quoted by Marey in his work on "The Flight of Birds." Marey himself, however, concludes that even this evaluation of the work is exaggerated. He says: "Reason, as well as experience, shows that the bird does not fall during the lowering of the wing. We can therefore assign to the fall of the bird only about the half of a revolution of the wing, or one-tenth of a second. . . . With this correction the fall of the bird is reduced to 0.049 meter five times per second, or 0.245 meter in one second."

But actually even Marey's estimate is exaggerated. Langley says that viscosity is negligible, and his statement has been widely quoted and seems to be generally accepted. But viscosity cannot be neglected, for it is only through viscosity that a moving plane takes hold of a

vein of air of more than its own width; and therefore a consideration of viscosity is necessary as a basis for Langley's own theory of the supporting power of the inertia of the air.

I find for the air pressure on 1 square meter of normal surface, moving with a velocity of 1 meter per second,

at 16° C., $k\Delta P = 0.082$ kilogram per square meter,

at 0° C., $k\Delta P = 0.076$ kilogram per square meter,

each from twenty-two observations. The figures are a little smaller than they would be for sea level, because the barometer was below normal. Now hot air is lighter than cold air and, other things being equal, should give less pressure. It will be seen that, on the contrary, $k\Delta P$ is larger for hot air. The reason is because viscosity is greater at higher temperature, and thus the plane grasps more air.

The unit of time which ought to be taken in Babinet's computation is the time required to transfer the weight of the bird from one mass of air, to which motion is being imparted, to a new mass not yet affected. The distance between these masses depends on wing dimensions. It is relatively less for a narrow wing. The time of transfer depends also on the velocity, and the time-unit in question, or what may be called the natural time-unit for flight, is shorter the greater the velocity and the narrower the wing. Thus at very high speeds the need of exertion for lifting the weight becomes vanishingly small, and at the soaring speed it changes sign.

Langley computed the skin friction of the air on a moving plane by a formula given by Maxwell, and concluded that it must be very small. He says: "There is now, I believe, substantial agreement in the view that ordinarily there is no slipping of a fluid past the surface of a solid, but that a film of air adheres to the surface, and that the friction experienced is largely the internal friction of the fluid, *i.e.*, the viscosity. Perhaps the best formula embodying the latter is given by Clerk Maxwell in his investigation on the coefficient of the viscosity of the air. This is $[\eta =] \mu = 0.0001878\ (1 + 0.0027\theta)$, μ and θ being taken as defined in his paper on the dynamical theory of gases in *Phil. Trans.*, 157. By this formula the actual tangential force on a 1-foot square plane, moving parallel to itself through the air at the rate of 100 feet a second, is 1,095 dynes (0.08 poundals), or less than one-fiftieth of 1 per cent. of the pressure on the same plane moving normally at this speed, and hence theory as well as observation shows its negligibility" ("Experiments in Aërodynamics," footnote, page 9).

I shall presently consider the applicability of the formula to the problem; but, waiving this consideration for the time being, we may note that the numerical value of the coefficient of viscosity is probably a little smaller than that given by Maxwell. The best experiments give values of the coefficient (η) for air from 0.000172 to 0.000178 in C. G. S. units at 10° C. Assume $\eta = 0.000175$. Then for a 1-foot square plane (both faces) the area (A) is 1,858 square cm., and a velocity (V) of 100 feet per second is 3,048 cm. per second, giving the energy necessary to overcome the pressure of viscous resistance, if $F = \eta A V \times f(a)$, where $f(a)$ is a function of the relative linear dimension of the plane in the line of sight, or what Langley has called the "aspect" of the plane, which is unity for a square plane,

$$F = 0.000175 \times 1{,}858 \times 3{,}048 = 991 \text{ ergs},$$

which is not essentially different from the value given by Langley.

It will be observed that no factor appears in this formula for the linear depth of the viscous layer (l). In theory the expression is to be divided by l, and in the dimensional formula for viscosity, $\frac{M}{LT}$, this division by L is indicated; but determinations of viscosity derived from the flow of gases through small capillaries in which l is very small, and those from the decrement of oscillating plates separated by much larger distances, are so nearly the same, that the effective depth demanded by the theory is evidently one of microscopical dimensions far within the depths of the experimental layers, and thus l is included in the numerical value of η determined by experiment. The process of molecular transfer of energy must be many times repeated within the experimental layer, and as long as the operation is fairly uniform throughout the layer, so that the velocity in a capillary tube increases regularly from the wall to the longitudinal axis of the tube without the formation of complex vortices and striæ, which only happens at low speeds, there is no need to consider the linear depth of the layer.

The case becomes different in dealing with extensive surfaces of superposed aëroplanes moving at high velocities, generating embracing stream-line envelopes of air in complex, vortical motion. Here the effective radius of the disturbed condition of the air is of importance. A narrow plane, say 2 inches wide, presenting the aspect of its longer dimension, creates by its motion through the air a region of vortical disturbance perhaps 2 feet wide — in fact, presumably much wider if

we consider the totality of minute motions constituting the wake; but the distances given are sufficient for practical considerations.

I may refer to an experiment by T. E. Stanton [1] in which a 2-inch square disk in an air current through a tube 2 feet in diameter just began to experience reaction from the walls of the tube. Langley found that superposed, horizontal, or only slightly inclined planes did not interfere so long as they were separated by vertical distances equal to their dimension in the line of flight. This, however, does not give the depth of the total disturbed layer, for the air shell controlled by the combined system extends to much greater distances.

The formula for viscosity is not as simple as the equation just given would indicate. It might have been surmised that if the viscosity of air is due to collisions of molecules, it would be influenced by the density of the air, since the mean length of the free path depends on the density. On the contrary, there is no influence whatever. This can only mean that the molecules are so nearly completely elastic that, the number of transfers in the layer being finite, it makes no difference how many times they collide in the given space. The transfer of momentum from one part of the gas to another is perfect, in so far as it depends on simple motions of individual molecules, and is only disturbed by the motion of air currents which may be highly irregular.

The salient fact in regard to gaseous viscosity is that it varies with the absolute temperature, that is, with the molecular velocity; not, however, with the first power of the temperature, as Maxwell supposed. Professor Holman obtained for air the formula,

$$\frac{\eta_t}{\eta_o} = 1 + 0.002751t - 0.00000034t^2$$

between the temperature limits 0° and 100° C., t being the centigrade temperature. This result shows that viscosity increases with the temperature, but at a diminishing rate, the reason for the diminishing rate being, as Sutherland shows,[2] that the spheres within which collisions must occur, owing to the perturbations of molecular attraction, are smaller at the higher molecular velocities. The same cause affects the mean free path of the molecules independently of its variation from change of density.

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[1] Institute of Civil Engineers, Proceedings, 136, 3 (1903).

[2] W. Sutherland, "The Viscosity of Gases and Molecular Force," Phil. Mag., Series 5, 36, 507 (1893).

In the formula which has been given above for air friction, V, the velocity, appears in the first power. If we confine our attention to internal friction of the air and let $v =$ *molecular* velocity, Sutherland demonstrates that, while the viscosity effect would vary as the first power of v if the molecules had no attraction for each other, the number of molecular impacts is increased by the deflection of molecules through their mutual attraction when at close quarters. On this account the exponent of v must be increased to at least 1.5 for air. In Meyer's formula,

$$\eta_t = \eta_o(1 + \alpha t)^n,$$

where η_t and η_o are the coefficients of viscosity at temperatures t and 0°, α is the coefficient of expansion, t the centigrade temperature, and n a number to be determined by experiment, Holman found $n = 0.77$. Since absolute temperature is proportional to the square of molecular velocity,

$$\eta \propto T^{\frac{3}{4}} \propto v^{2\times\frac{3}{4}}.$$

This is close enough for a first approximation, since n varies slightly with the temperature.

The velocity on which internal friction depends is that of the gaseous molecules, in comparison with which the moderate speed of an aëroplane may be neglected. In taking an equation, originally derived from the theory of molecular motions and dealing with microdimensions, and transferring it to macrodimensional motions, there is opportunity for discrepancies to arise. The viscous resistance has not hitherto been distinguished from the skin friction, which includes the infinitesimal slip of the air on the solid surface as well as the slip of an enormous number of successive air layers on each other, because they are inextricably entangled. Although the internal friction of the air is practically independent of the velocity of the aëroplane, the slip of the air on a solid surface, or, what amounts to the same thing, on an adherent film of virtually "solid" air, is not unaffected by changes of speed. As the speed increases, the slip of successive air layers on one another is relatively less, and the sustaining power of an aëroplane or the thrust of an air propeller become greater, the higher the speed. It is the variation of surface slip, or rather of the slip of successive air layers parallel to the surface, which we measure in experiments with air propellers moving at varying speeds. Both the portion of air immediately struck by a moving inclined plane, and that on which motion is less directly impressed through internal friction, receive momentum from

the moving solid, transferring the pressure of the heavy solid to an extensive body of air, whose horizontal area increases with the speed, thereby greatly increasing the efficiency of the aëroplane as a supporting body. Eventually, as speed still further increases, slip will presumably cease entirely; but the air will then behave as a rigid body, *more* power will be needed to force the plane through the air, and its supporting efficiency, after reaching a maximum, must diminish at still higher speeds. When slip ceases, the interaction between the aëroplane and the air through which it moves consists in a transfer of a certain amount of momentum per unit of time to a definite mass of air. The mass of air affected is proportional to the velocity, and so is the momentum. Consequently the energy expended is proportional to the square of the velocity; but where there is slip, less momentum is transferred, and the energy involved is proportional to a power of the velocity less than the square.

Dr. A. F. Zahm[1] has experimented with pine boards, 25½ inches wide and 1 inch thick, in a tunnel 6 feet square, the suspended boards being exposed to air currents flowing parallel to their lengths at speeds between 5 and 40 feet per second, obtaining the tangential force from combined skin friction and internal friction of the air when the linear dimension (l) in the line of flow varies between 2 and 16 feet. For a square plane the measures give a tangential stress of 0.00052 pounds per square foot, for $V = 10$ feet per second. If A is the area of the plane (both faces), a the aspect or ratio of the dimension of the plane in the line of motion to its transverse dimension, and V the velocity of the plane, the total friction in C. G. S. units is,

$$F = 0.0000632 A a^{-0.064} V^{1.85}.$$

For a turbulent current the slip appears to vanish and the exponent of V becomes 2. This formula contains no factor for depth of air layer, evidently because the section of the tunnel exceeded the effective dimensions of the active layer.

The progress attained in researches on viscosity has been through a series of imperfect conceptions, including some misconceptions, and their partial rectification. The supposition that *molecular* velocity enters as the first power into the equation was a misconception; but owing to slip, experiments were satisfied for low velocities by taking

[1] "Atmospheric Friction on Even Surfaces," Phil. Mag., Series 6, 8, 58 (1904).

an equation of the same form and letting V, the surface velocity, enter as the first power. With higher velocities (meters per second instead of millimeters per second), V becomes $V^{1.85}$, and when the motion is highly turbulent, V^2. A more complete molecular theory also indicates that in the formula for internal friction the molecular velocity appears as $v^{1.5}$. To take a formula devised to express the relation between a tangential stress and temperature, in which it might be permissible to substitute ***molecular*** velocity for temperature, if the formula were correct otherwise, and then to substitute surface velocity in place of molecular velocity, can only give an erroneous result.

Substituting Zahm's formula for Maxwell's in a recomputation of the energy needed to overcome the friction of a 1-foot square plane moving tangentially at a velocity of 100 feet per second, we get

$$F = 0.00000632 \times 1{,}858 \times (3{,}048)^{1.85} = 32{,}760 \text{ ergs},$$

which is thirty-three times as large as the 991 ergs given with the best values by the erroneous formula.

Maxwell's coefficient of viscosity and the values of η given in physical tables, such as those of Landolt-Börnstein (except under a special condition to be noted presently), are not absolute coefficients of the friction of a moving gas against a solid wall, but are relative numbers serving to connect the internal friction of the gaseous molecules with temperature for various substances. They can readily be converted into absolute coefficients of friction by comparison with that for air whenever the latter shall have been determined with sufficient precision.

It is important to note that in experiments on the flow of gases through tubes, the head, or pressure, required to produce a given velocity through an orifice, or through a short pipe whose friction may be neglected, must be distinguished from the difference of pressure needed to overcome the friction against the walls of a long tube. Let $\Delta P =$ difference of pressure per unit area of section at the ends of a tube of length l, $S = \pi r^2 =$ section of tube, $A = 2\pi rl =$ area of walls of tube, $V =$ linear velocity $=$ volume of flow $\div$ section, $F = S\Delta P =$ frictional resistance, $H =$ absolute coefficient of air friction on a solid surface. Then, accepting Zahm's determination of the exponent of V,

$$H = \frac{F}{A V^{1.85}} = \frac{r\Delta P}{2lV^{1.85}}.$$

From the values of air friction commonly accepted by engineers, given by Thomas Box in his "Practical Treatise on Heat" (page 117), I have selected various values and have computed from them the values of the absolute coefficient of air friction obtained by the preceding formula.

Diameter.	Section.	Velocity.	$H \times 10^6$.
Inches.	Square centimeters.	Centimeters per second.	
¼	0.316	1,491	8.58
⅜	0.713	662	7.59
¾	2.85	166	6.18
1	5.06	93	5.65
1¼	7.92	596	7.53
2½	31.7	149	6.09
4	81.1	582	7.46
8	324.0	146	6.04
12	730.0	647	7.59
24	2,918.0	162	6.17
36	6,566.0	719	7.69
60	18,241.0	259	6.60

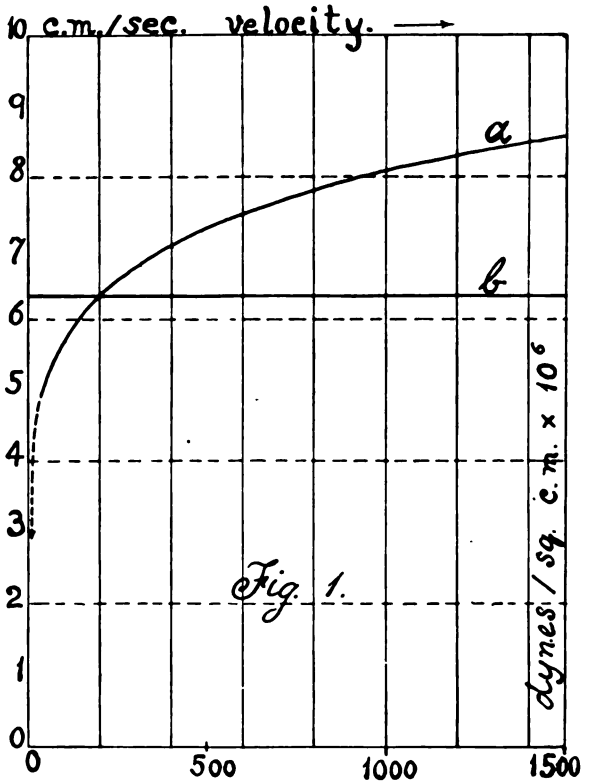
The value of H varies with the velocity from 5.6×10^{-6} for a velocity of 1 meter per second to 8.6×10^{-6} at 15 meters per second (Fig. 1, Curve *a*). Taking a mean of all of the values of H in the preceding table and comparing it with the value obtained by Zahm,

$H = 0.00000693$ from flow of air through tubes (Box),

$H = 0.00000632$ from flow of air over planes (Zahm).

The agreement between these values, in spite of the differences in the forms of the surfaces and in the methods by which they were obtained, guarantees the reliability of the result. The measures also lead us to expect a progressive divergence between the values of H given by the two methods at still higher velocities. Zahm's value, having been obtained with plane surfaces, is to be preferred for aëroplane problems. For such surfaces Zahm found that the coefficient of air friction is a

constant (Fig. 1, Curve *b*). It seems probable that this apparent constancy is due to the summation of two different effects, namely, the edge resistance and the skin friction, which interact in a reciprocal manner, their sum being a constant, while pure skin friction is to be represented by a curve. There is evidently a discontinuity in the *HV*



RELATION BETWEEN THE ABSOLUTE COEFFICIENT OF AIR FRICTION ON A SOLID SURFACE (II) AND THE LINEAR VELOCITY

a from measurements of flow through tubes. *b* from flow of air over planes. Abscissæ = velocity in cm./sec. Ordinates = stress in dynes/sq. cm. (× 10^6)

law at low velocities, and experiments are especially needed in this intermediate region. Osborne Reynolds has determined the limit of velocity at which turbulence begins for liquids moving through tubes of small diameter, and Couette (*Annales de Chimie et de Physique* [6], 21, 433) has done the same for moving surfaces of concentric cylinders, finding that, with surfaces separated by 2.5 mm., the frictional resist-

ance for velocities greater than about 90 cm. per second becomes proportional to the square of the velocity; but below this speed the frictional resistance varies as the first power of the velocity. Similar measures are needed for air to give the velocity at which the law changes.

Although the relation between viscosity and temperature represented by what may be called Maxwell's equation for η, $\eta = a(1 + bt)$, where a and b are numerical constants and t is the temperature, is independent of the air pressure, it does not follow that the momentum transferred from an aëroplane to the air[1] by virtue of the air's inertia and by means of viscosity is similarly independent of the pressure. It is hardly necessary to point out that the inertia of a given volume of air is proportional to its density, and that pigeons thrown out of a balloon at a great height are unable to fly in the rare atmosphere, but fall helpless. The value of H just given is for air of normal density. Other things being equal, the frictional resistance of the air to the motion of an aëroplane is proportional to the mass of air set in motion, which again depends upon the density of the air.

The distinction to be observed between the transfer of momentum from a solid to a fluid, and its transfer from one body of air to another, is that in the former case the momentum of the solid is that of a body in which mass and volume are proportional, and neither mass nor volume is dependent on air pressure; while for the air masses the volumes and pressures are in inverse relationship and the mass of a given volume varies with the pressure. The transfer of momentum from a moving solid to the air by means of viscosity is the imparting within a specified time of the momentum pertaining to a definite volume of solid substance to a much larger volume of air whose mass is *not* independent of the pressure. Here the amount of momentum transferred, other things being equal, is proportional to the density of the air; but the transfer of momentum from one portion of air to another is more easily accomplished if the air be rare (provided it is not so rare as to have entered on the ultragaseous stage of exceptionally large, free path), while the amount of momentum transferred is proportionally less, so that the result is independent of the density.

Dimensionally, viscosity is $\frac{M}{LT}$, and is a stress given in C. G. S.

[1] The momentum imparted to a particular body of air is handed on to other portions of the medium. It may be dissipated thermodynamically by diffusion and conduction, or the pressure may eventually be transferred to the surface of the ground or to the walls of a containing chamber. In any case the given momentum exists as such only temporarily in the fluid.

units in dynes per square centimeter. Multiplying by the area, we have $\left(\frac{M}{LT}\right) \times L^2 = \frac{ML}{T}$ to represent the momentum transferred through a surface from a moving solid to air, or *vice versa;* and this, multiplied by a velocity, gives $\frac{ML^2}{T^2}$ as the dimension of the work involved in overcoming the viscous resistance ($F = HAV$). If this were the whole process, the product, viscosity × area × velocity, would give the energy expended in producing the motion of an aëroplane; but a further and, in general, a very much larger amount of work has to be performed in generating turbulent motion of the air.[1]

Exception must be made to the law of gaseous friction founded on experiments on the flow of air at considerable speed, and to the absolute coefficient of air friction (H) appropriate to this motion whenever the speed is so slow that there is time for a complete redistribution of molecular velocities, and for the establishment of a stable and uniform gradient of speed within the depth of a layer of gas only a few times the length of the mean free path of the molecules. Under these conditions the viscous resistance is proportional to the velocity of the moving surface, and Maxwell's coefficient (η) applies.

A small drop of water falling through the air, under the attraction of gravity, increases its velocity until a maximum speed is reached, determined not by the mass of the drop, but by the area of its surface and the viscosity. This maximum velocity of fall, or, what is the same thing, the velocity of an upward air current which will just overcome the downward pull of gravity and maintain the drop suspended at a constant height, is given by a formula due to Sir George G. Stokes,[2]

$$v_{max.} = \frac{2}{9} \frac{gr^2}{\eta},$$

[1] As was recognized by Stokes in the footnote to p. 99, Vol. I. of his collected papers.

[2] The original equation is contained in the great memoir by Stokes, "On the Effect of the Internal Friction of Fluids on the Motion of Pendulums," in the Transactions of the Cambridge Philosophical Society for 1850, and may be found in his Mathematical and Physical Papers, 3, 60, equation 127,

$$V = \frac{2g}{9\mu'} \left(\frac{\sigma}{\rho} - 1\right) a^2,$$

where g is the force of gravity, a the radius of the sphere, σ and ρ the densities of water and air, respectively, and where μ' is what Stokes calls the "index of friction," being what we now call the "coefficient of viscosity," divided by the density of the fluid. Since the date of this memoir it has been proved that the viscosity of compressible fluids is independent of the pressure. Consequently it is now appropriate to give the formula in an emended form. The factor $(\sigma - \rho)$ differs so little from unity that it may be omitted, as I have done in the text.

in which g is the acceleration due to gravity, r the radius of the drop, and η is Maxwell's coefficient of viscosity. If $\eta = 0.000175$,

$$v_{max.} = 1.246 \times 10^6 \times r^2.$$

This agrees well enough with observation for spheres up to about $\frac{1}{10}$ mm. diameter, but only for spheres which do not exceed this size. Larger ones must be treated by formulæ for pressure similar to those for a normal plane of equal circular section, with a factor of one-half for rotundity, adding a viscosity term which becomes less and less important as the size of the drop increases.

It can be shown from the experiments of Poiseuille that the linear velocity of flow of water through a fine capillary tube, where the velocity is so slow that there is no slip on the wall and no turbulent motion, may be represented by the equation,

$$v = \frac{r^2 \Delta P}{8\eta l},$$

where r is the radius of the tube, ΔP the difference of pressure at the ends of its length (l), and η the viscosity, and the same equation serves equally well for the flow of a gas. Here again Maxwell's coefficient gives results which are correct, but if we attempt to extend the application of the formula to include such results of engineering practice as those for large tubes and considerable velocities, which have been given above, we shall find that η must be increased between twenty and thirty times for a $\frac{1}{4}$-inch tube and still more for larger sizes, which agrees with the preceding demonstration of the inapplicability of the Maxwell coefficient to the conditions of the soaring aëroplane. The linear velocity of air flowing rapidly through tubes of large section is given by the equation,

$$V^{1.85} = \frac{r \Delta P}{2Hl}.$$

I have for some time recognized that Langley was wrong in neglecting viscosity, and in a lecture delivered before the Boston Scientific Society in February, 1908,[1] I demonstrated that viscosity is not only *not* negligible, but that it is most intimately involved, indeed is the very foundation of Langley's own theory, since if it were not for viscosity it would be impossible for a soaring aëroplane to virtually "take hold

[1] Reported in the Boston Transcript for February 27, 1908.

of" a body of air of many times its own extent and be held up by the inertia of the air.

In the case of an unsupported horizontal plane carried in a horizontal direction through the air there is no force developed which can produce upward motion at any speed. The case is therefore different from that of an inclined plane, which reverses its vertical motion at the critical soaring speed. The horizontal plane can have its rate of fall diminished indefinitely as the speed increases, but without the rate ever becoming zero.

If an aëroplane in calm air is standing still, its fall will be resisted by the minute amount of air friction given by the theory, calculated for the natural unit of time, the plane taking hold of a shell of air which surrounds it on every side, except to the extent that discontinuity may be produced by slip; but let the plane move along rapidly and motion is communicated successively to a large number of similar air shells, the total resistance to the fall being equal to the sum of the support offered by the individual air shells, whose number depends upon the effective distance of propagation of the viscous resistance during the time of passage of the plane.

At the speeds we have used, the gas molecules have time to move out to a distance of several feet as the plane passes, but the Langley multiple plane experiment indicates that the effective air shell is comparatively shallow. The principal part of the air support is derived from molecular collisions in the intricate, interlacing paths within a short distance from the plane. The unit of time to be employed is the time needed to transfer the motion of the plane to the *effective* air shell — a very small fraction of a second. At the beginning of motion from a state of rest, the supporting air shell is of zero depth. The depth of the shell continues to increase as relative motion is imparted to the solid and its surrounding medium, successively more and more remote layers of air being brought under the viscous control until the maximum depth possible for the given velocity and viscosity is reached. Time is required for the development of the system, as well as for its continual reproduction. The inertia of the air shell is small compared with that of the heavy aëroplane, but the energy transferred is the kinetic energy developed in the plane by gravity during the interval of time needed for its transfer to the air, which is exactly equivalent at the soaring speed. This natural time interval, or transfer time of an equivalent energy, is of course a variable quantity, becoming

shorter as the temperature rises and the molecular collisions within a given space become more numerous.[1] If the speed is doubled, the plane remains in a given region of the air only half as long, the air molecules can only move half as far, the dimensions of the supporting air shells are half as great, or there are twice as many of them as before in the same length of path. If the effective air shells were no more numerous than before there would still be twice as many individual shells threaded in a unit of time at the double velocity, and with twice as many individuals in the unit of length the air effect will be four times as great at double the velocity. The time of fall (t) of a horizontal plane through a space ($s = V_o t_o$) is therefore given by the formula,

$$t = t_o + t_1 V^2,$$

where V is the horizontal velocity, V_o is the velocity of fall for $V = 0$, t_o is the time of fall for $V = 0$, and t_1 is a constant, or nearly a constant time interval, varying only slightly with change of temperature of the air.

In a series of experiments with a horizontal plane of 30 inches transverse dimension and 4.8 inches in the line of flight, exposing a horizontal section of 1 square foot, I obtained with the Langley plane dropper at different speeds, times of fall through a space $s = 1.22$ meters, which are represented by the formula,

$$t = 0.5 + 0.00278\, V^2,$$

V being given in meters per second.

Speed of Plane.	Time of Fall.
0 meter per second	0.5 second $= 0.5 + 0.0$
6 meters per second	0.6 second $= 0.5 + 0.1$
12 meters per second	0.9 second $= 0.5 + 0.4$
24 meters per second	2.1 seconds $= 0.5 + 1.6$
48 meters per second	6.9 seconds $= 0.5 + 6.4$

Let us suppose, for example, that the effective diameter of a supporting air shell in the direction of the line of flight at the highest speed was ½ meter for this plane, or that, at least virtually, the support was transferred to a new mass of air ninety-six times per second.

[1] In the absence of viscosity the process would have no limit save that given by the boundary of the atmosphere, and the natural time interval would be greatly extended.

Then the space fallen through during the time of the first transfer was $s = \frac{1}{2}gt^2 = 0.53$ mm., the total distance fallen in 6.9 seconds being, as in the other cases, 1.22 meters.

Langley's one-fiftieth of 1 per cent. is not a bad estimate of the retardation by the air in a fall of ½ mm. from a state of rest, but at the speed which he took for his illustration, 100 feet per second, we should have, instead of a skin friction of 0.0002, a resistance due to internal friction of the air and skin friction equal to many times this quantity. At the highest speed of the preceding table, for example, we might expect a resistance from internal friction of the air and skin friction equal to $96 \times 0.0002 = 0.0192$, and it is probable that the viscosity effect is a quantity of this order, although considerable uncertainty remains as to the dimensions of the effective air shell. Zahm's experiment, allowing something for slip, favors the supposition that the effective supporting air shell may have been a little over 1 meter in length.

If we let $\Lambda =$ the number of transfers to fresh air masses per second, the natural time interval or time of transfer to which I have alluded is $1/\Lambda$. Besides varying with the speed, the quantity Λ, to which the supporting power of an aëroplane is directly proportional, varies greatly according as the plane meets fresh layers of air, or air which has already been disturbed by some antecedent member of a train or by a previous movement of the same member. If the air has previously been set in motion in such a way that it tends to slip away from the advancing aëroplane, the latter loses its grasp on the air to this extent. Such an antecedent disturbance may be either advantageous or disadvantageous. In the flapping of a bird's wing advantage is taken of the result of a previous motion by a suitable alteration of the angle of the wing plane. With a plane at a fixed angle, all previous disturbance of the air is disadvantageous. In actual aërodromics the condition of turbulence in the air will no doubt be the usual one, and plans must be laid accordingly. A large-scale turbulence of the air may be disastrous in its consequences, but intricate, interlacing vortices on a small scale ought to increase the internal friction and give a plane a better hold on the air.

The viscosity resistance cannot increase as the square of the velocity when the speed approaches that of sound, nor at low speeds where there is much slip, but the exponent 2 is about right for medium velocities, at least where there is turbulence.

While aërial friction will retard the velocity of an aërodrome at very high speeds, and will thus limit the attainable speed, skin friction is essential to the efficiency of an aërodrome, and up to a certain point the greater the skin friction the better is the grasp on the air and the larger is the sustaining power.

WESTWOOD, MASS., July, 1908.

APPARATUS AND EXPEDIENTS IN THE BACTERIOLOGICAL LABORATORY

By STEPHEN DeM. GAGE, S.B.

In the modern Public Health Laboratory the time of the scientific staff is largely occupied by routine work, and, an increase in the laboratory force being impossible, it is often a difficult problem so to arrange the work that attention may be given to the special investigations which are so necessary to keep the laboratory in touch with modern progress. The solution of this problem usually lies in a thorough systematization of the routine, and in the installation of time-saving devices and other apparatus specially adapted to the work. In many instances the infinite number of minor details of which bacteriologic technic is composed, and the opportunities for time saving a close study of those details will show, are not recognized. An illustration of this may be drawn from a recent investigation at Lawrence of the pollution of shellfish, in which tests for *B. coli* and the sewage streptococcus were required on the shell-water and intestines of from two to ten individual clams or oysters from a large number of sources. In the process of making these tests, a total of over 400 distinct manipulations were required in the analysis of each clam, exclusive of those incidental to the preparation of media, cleaning and sterilizing apparatus, and recording and reporting results. When we multiply this total by the number of samples examined, it is readily seen how a slight change in the technic, the elimination of superfluous motions, or the introduction of some time-saving device or specially designed apparatus may result in a material saving of time.

At the Philadelphia meeting of the Society of American Bacteriologists, in 1904, the writer described informally some of the methods, expedients, and special apparatus in use at the Lawrence Experiment Station of the Massachusetts State Board of Health, and recent requests for information indicate that many of these features are practically unknown elsewhere, and may be of sufficient interest to warrant their publication at this time. The various devices described have been

evolved from suggestions by members of the laboratory force, or have been copied or modified from those in use in other laboratories. Since, in many instances, the originators of the ideas are unknown to the writer, and it is impossible to give due credit to all, they are presented merely as types which have proved their usefulness at Lawrence.

Laboratory Equipment.—In equipping a laboratory, usefulness and durability should be the primary consideration, and, wherever possible, apparatus which is to receive hard usage should be made of metal, rather than of glass. Glassware, especially test tubes, should be sufficiently strong to stand rough handling. The first cost of thin tubes is less, but the loss from breakage is much greater than with heavier tubes, and the operator unconsciously wastes considerable time in the effort to prevent this breakage.

A sufficient stock of all common glassware and supplies to meet any possible emergency should be carried in stock. All common glassware should be cleaned as soon as received, and stored in a clean, dust-proof place, while sample bottles, Petri dishes, etc., should be sterilized and wrapped in paper, or placed in dust-proof boxes ready for instant use. Nothing causes so great a waste of time during a rush of work as a shortage of apparatus. About three-fourths of the cost of operating a bacteriological laboratory is expended in salaries, and a proper and plentiful equipment will pay for itself many times over in the increased efficiency of the laboratory assistants.

Method of Cleaning Apparatus.—All glassware, bottles, tubes, plates, pipettes, etc., are soaked over night or boiled for half an hour in a strongly alkaline permanganate solution, rinsed, treated with oxalic acid, and then washed five times with water. The alkaline permanganate followed by the oxalic acid is a far more satisfactory cleaning agent than is chromic acid, and the former is a waste product from the ammonia distillations in many water laboratories. The oxalic acid is used as a saturated solution to which about 2 c.c. commercial sulphuric acid per liter is added. The permanganate solution contains about 8 grams potassium permanganate and 40 grams caustic soda or potash per liter, and is diluted with ten to twenty parts of water for use. If the strong solution of permanganate is boiled thoroughly before use it is less likely to stain the hands. Both permanganate and oxalic solutions ready for use are conveniently kept in large, wide-mouthed crocks. Tubes containing solid media, and plates containing gelatin, are boiled out with water before being treated with the cleaning fluids, but only a preliminary

rinsing is necessary for tubes containing fluid media and plates containing agar. Tubes to be cleaned are placed on end in straight-sided enameled dishes, a sufficient number of tubes being used to completely fill the dish, and all operations of cleaning carried out with the dishful of tubes handled as a unit, the dish being dipped into the crocks of cleaning solutions and into a large dish of water in washing, the tubes being kept in place when the dishes are emptied by a circle of wire netting placed on top. After washing, the wire netting is removed, the dishful of tubes inverted upon a towel, the dish raised about 3 inches and a strong rubber band slipped about the block of tubes, thus holding them in place so that the dish can be removed. Tubes placed in this way dry more quickly than when placed in draining racks, the water being absorbed by the towel, from which it evaporates rapidly. When dry, the whole block of tubes may be transferred to the storage drawer before removing the rubber band. Petri dishes are handled in much the same manner, bottoms and covers being placed in separate dishes during the cleaning operations, and kept separate until dry and ready to be matched up for use. Fermentation tubes, the simple bent tubes without foot are most convenient, are packed in wire baskets holding about forty tubes, and the basket of tubes handled as a unit. A tall glass cylinder filled with permanganate solution stands upon the planting table, in which pipettes are placed as soon as they have been used, the operations of cleaning and washing the pipettes being completed in the cylinder, after which the surplus water is shaken from the pipettes and they are transferred without further drying to the metal boxes in which they are sterilized and stored.

For washing bottles it is desirable to have a bottle washer. Two of these are in use at Lawrence, one for large bottles, and one on which eight small bottles may be washed at one time. The jets on the small washer are arranged in two sets of four each, so spaced that four bottles may be picked up and placed on the washer with one hand in one motion. Both washers are connected with the city water mains by swivel joints, in order that they may be swung back against the wall when not in use, and have shut-off cocks with long handles for controlling the flow of water.

Labeling Media.—When a number of different media are used in a laboratory it is advisable to have some quick and ready means of distinguishing one from another. While the use of written labels may serve this purpose, much time will be wasted in their use, since each

basket of media must be labeled separately, and unless marked very conspicuously such labels must be examined at close range. At Lawrence written labels have been entirely dispensed with, the different media being distinguished by the use of different sized tubes and by cotton plugs of different colors.

All solid media are placed in tubes 6 inches long by about ½ inch diameter, while all fluid media are placed in tubes 5 inches long by about ⅜ inch diameter. After the medium is tubed, a solution of dye is sprayed upon the plugs with an atomizer, a distinctive color being used for each medium. For example, gelatin and nitrate solution are colored red, lactose agar and Dunham's solution are colored blue, etc., the distinction between the gelatin and the nitrate solution, and between the lactose agar and the Dunham's solution, etc., being made by the different size of the containing tubes. The dyes penetrate the cotton to such an extent that the distinctive color may be readily recognized even after the cotton plugs have been flamed. The use of jewelers' cotton of different colors has been suggested for the same purpose, but this requires that tubes of different colors be kept separate before filling with media, while by the use of the dyes all tubes are plugged with raw cotton and are available for any media for which they are suitable. For applying the dyes, the small metal atomizer used by artists to fix charcoal drawings is preferable to druggists' atomizers, being readily cleanable, only one being necessary, irrespective of the number of colors employed. Media marked in this manner are readily distinguished across the room or in the darkest corner of the incubator or storage closet, while with written labels the basket of media must be removed to the light or one must cross the room to inspect the label closely before the media can be identified.

Pipettes.—For use in a water laboratory, where a large number must be handled daily, the bulb pipettes furnished by apparatus dealers are far from satisfactory. Owing to the projecting bulb they cannot be readily drawn from the box in which they are sterilized and stored without danger of pulling out one or more upon the table or upon the floor, and when handled in bulk during cleaning and sterilizing the breakage is excessive. For a number of years straight pipettes made in the laboratory have been used at Lawrence with entire satisfaction. Two sizes are in general use, both 10 inches long, made from No. 3 tubing, one calibrated to deliver 1 c.c., and the other calibrated to deliver either 1 or 2 c.c., the latter being made with a slight lip, in order that

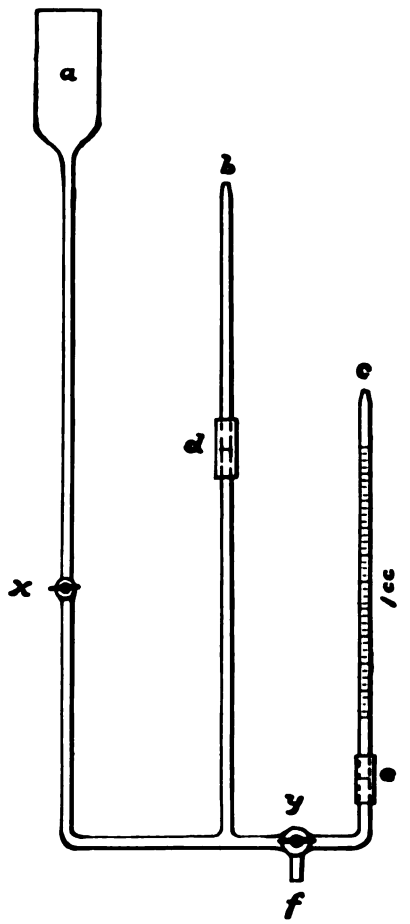


FIG. 1.— APPARATUS FOR CALIBRATING PIPETTES

the two sizes may be readily distinguished when contained in the same box. It is convenient also to have a few pipettes made from larger tubing and calibrated to deliver 10 c.c. Both large and small pipettes are calibrated in the apparatus illustrated in Figure 1, the operation being as follows: The apparatus is filled with mercury, the meniscus carefully adjusted to the lower mark in the capillary pipette *c*, and both stopcocks closed. An uncalibrated pipette *b* is inserted at the slip joint *d*, and the cock *x* opened until it is entirely filled with mercury, when cock *x* is closed and the three-way cock *y* opened, allowing the mercury to flow from *b* until it rises to the upper mark in the capillary pipette *c*,

the level to which the mercury has fallen in *b* being marked with a fine file. The mercury is then drawn from the pipette *b* and down to the lower mark in the capillary pipette by means of the three-way cock, flowing out through the waste vent *f* into a beaker, whence it is returned to the reservoir *a* as necessity requires. By means of the slip joint at *e* the capillary pipette may be removed and one of larger capacity inserted when it is desired to calibrate large pipettes. In an earlier form of calibrating apparatus, which has already been adopted into some other laboratories, the capillary pipette was omitted, the mercury being drawn from the uncalibrated pipette into a beaker placed on the scales, the volume being determined by the weight of mercury withdrawn. With the apparatus illustrated calibrations can be made much more rapidly than with the older type, and the accuracy is fully as great. If preferred, instead of marking the calibrations with a file, the pipette may be coated with paraffin and the mark made in this, the calibration being afterward etched in with hydrofluoric acid. The objection that file-marked pipettes break more easily than those which are etched appears to be theoretical rather than practical, however, and file marking is much quicker. The time consumed in making pipettes in the laboratory is small, and is more than offset by their convenience and the low rate of breakage. The average laboratory assistant can make and calibrate the 1 c.c. pipettes at the rate of two to three dozen per hour with a little practice.

Dilution Bottles.—In the analysis of sewage, milk, and many waters, dilution of the sample with sterile water is necessary before plating, the water for dilutions being usually measured out into flasks or bottles before being sterilized, and the actual volume measured after the dilution has been made. For this purpose the green glass bottles commonly used by liquor dealers, called registered flasks, are less liable to be broken, and fully as convenient as the more expensive Erlenmeyer flasks or laboratory bottles commonly used. Two sizes of these are used at Lawrence, a half-pint size containing 99 c.c. of water, and a quart size containing 499 c.c. of water. By using both 1 and 2 c.c. pipettes, and combining the bottles in various ways, a great variety of dilutions are available. The use of 2 c.c. pipettes, in this case, introduces a small error, but as the probable error of any quantitative bacteriological analysis is about 5 per cent., this small error may be neglected. The bottles are filled with a definite amount of water, plugged hard with cotton, and sterilized in the autoclave. During sterilization, a certain amount of water is lost, but if care be taken to always operate the auto-

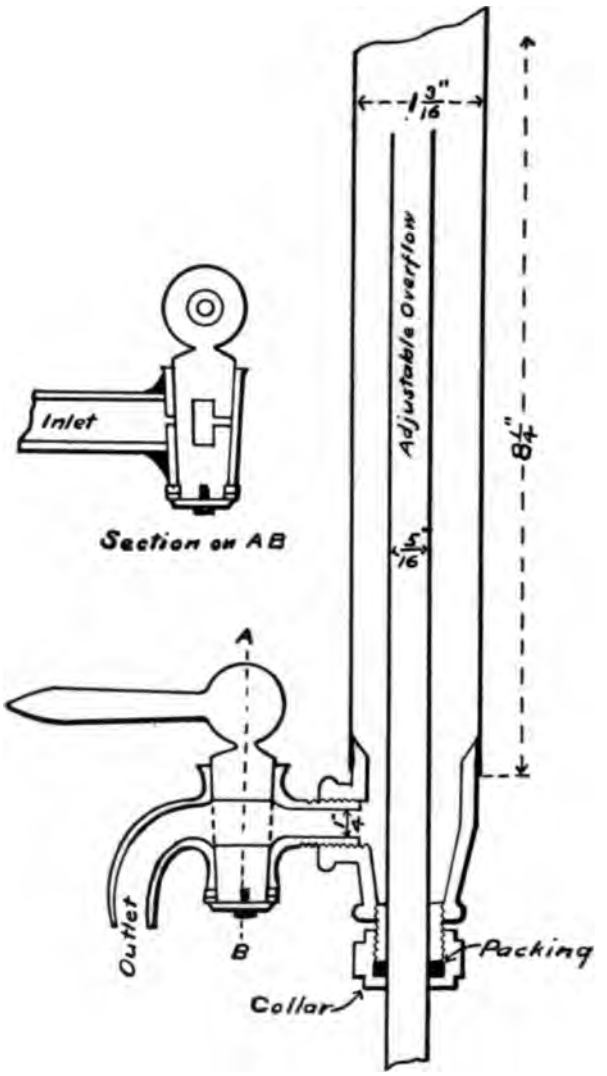


FIG. 2. — AUTOMATIC APPARATUS FOR FILLING DILUTION BOTTLES

clave in exactly the same manner, this loss will be constant and can be corrected for when filling the bottles, thus doing away with the necessity of measuring the volume in each bottle when the dilution is made.

For filling dilution bottles, the apparatus illustrated in Figure 2 will be found to effect a considerable saving of time when a large number must be filled daily. This consists of a reservoir in which the water is

measured, an overflow tube by which the volume is regulated, and a three-way cock which serves both to fill and empty the reservoir. The overflow tube passes up through a packed joint into the reservoir, and may be moved up and down while the apparatus is being calibrated to deliver the required volume of water, after which it is locked securely in position by tightening the collar through which it enters. The side arm of the three-way cock is connected directly with the city pressure by a long arm, a swivel joint permitting the apparatus to be swung back against the wall when not in use. The orifice through which the water enters the three-way cock from the city mains should be quite small, about $\frac{1}{32}$ inch for a pressure of 60 pounds, otherwise the pressure will throw the water out of the reservoir. The apparatus is made entirely of brass pipe fittings, and can be constructed by any first-class tinsmith at a cost of two to three dollars. If trouble is experienced in obtaining a proper three-way cock, one may be readily made from an ordinary lever faucet by boring a hole through the side and soldering on a side arm, this being the form shown in the illustration.

Counting Colonies of Bacteria.—It is often necessary in water or milk analyses to enumerate separately the total number of colonies on a plate and the number of each of one or more types, as, for example, the total number and the number of liquefiers on gelatin plates, or the total and red colonies on litmus-lactose agar plates. It is the custom of most bacteriologists to make such counts separately, going over the plate two or more times for the purpose. It is quite possible, however, to make two counts at the same time by carrying the total count mentally and recording the special colonies as they appear under the counting lens upon a mechanical tally or lumber counter. With a little practice, double counts made in this way are fully as accurate as are two separate counts, while the total time required for counting is reduced nearly one-half, in addition to the relief from eye fatigue which is the usual accompaniment of a large amount of routine counting.

Transportation of Samples.—Samples of water for bacterial analysis which are collected at a distance from the laboratory must be packed in ice during transportation. For this purpose shipping cases consisting of a wooden box with an inner metal compartment for the sample bottles have proved serviceable at Lawrence. The boxes are made from thoroughly dry pine lumber, which has been filled with paraffin to prevent warping, and all joints are made with screws to facilitate replacing any part which may become broken. The construction is shown in

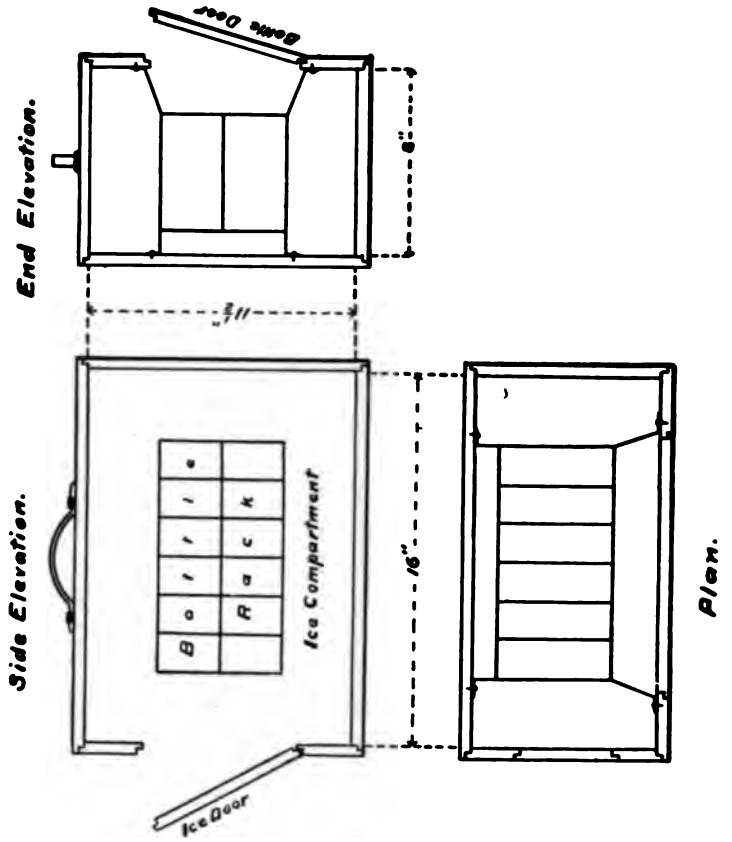


FIG. 3.—CASE USED BY MASSACHUSETTS STATE BOARD OF HEALTH FOR SHIPPING SAMPLES OF WATER FOR BACTERIAL ANALYSIS

Figure 3. Before collecting samples, the outer compartment surrounding the samples is filled with a mixture of about equal parts of sawdust and ice, broken to the size of a hen's egg. The sawdust is sent out with the cases, as it is often difficult to obtain in the field. Samples packed in this manner may be kept at a temperature of about 40° F. for twenty-four hours or more, and analyses obtained which will be sufficiently accurate for all practical purposes. For this work, 8-ounce tall Blake bottles with glass stoppers are used, it having been found by experiment that there is less change in the bacterial content of water in bottles of this size than in smaller bottles. After sterilization, the bottles are capped with paper caps held in place by rubber bands, wrapped in heavy glazed manila paper and sealed, the wrapper protecting the bottle from

breakage during transportation and from contamination by dust and dirt when stored for some time before use. When collecting samples, the paper wrapper is either removed and replaced or is merely torn away from the neck of the bottle, at the option of the collector. The bottles, wrappings, etc., are well shown in the photograph, Figure 4.

A Thermo-Regulator.—It sometimes happens that the temperature regulator for an incubator is broken, and some delay must ensue before a new one can be obtained. In such an emergency a regulator similar to the one shown in Figure 5 was tried a number of years ago, which proved so satisfactory that the one illustrated was placed permanently

FIG. 4.—PHOTOGRAPH OF SAMPLE CASE SHOWING WRAPPED BOTTLES

on the 40° incubator. This is a modification of the well-known Dunham regulator, consisting of a large bulb filled with alcohol connected with a long U-tube filled with mercury. Passing through a T into the open end of the U-tube is a smaller tube, adjustable with reference to the height of the mercury, through which the gas passes into the burner, the flow of gas being regulated by the expansion and contraction of the alcohol acting on the mercury column. A by-pass with a small stopcock admits sufficient gas to the burner to maintain a pilot flame at such times as the flow through the adjustable tube is cut off. In the permanent apparatus illustrated, only those parts coming in contact with the mercury are of glass, the rest of the apparatus, except the flexible connection, being of brass, small gas fittings being used wherever possible.

An emergency regulator may be made up on these lines in an hour

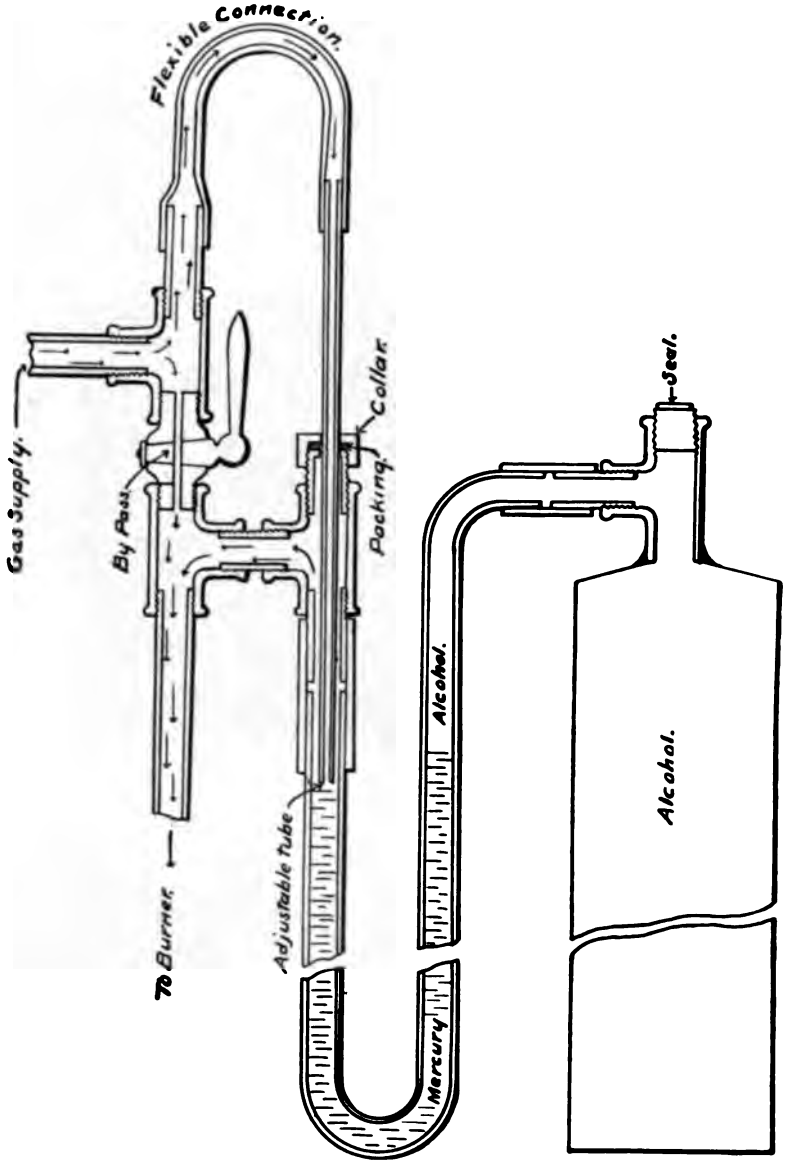


FIG. 5. — THERMO-REGULATOR USED ON 40° C. INCUBATOR AT LAWRENCE EXPERIMENT STATION

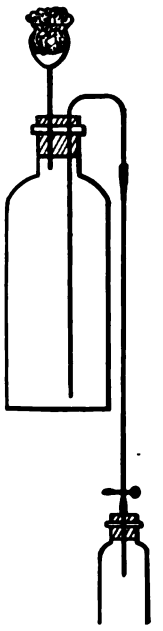


FIG. 6. — WASH BOTTLE FOR STERILE WATER

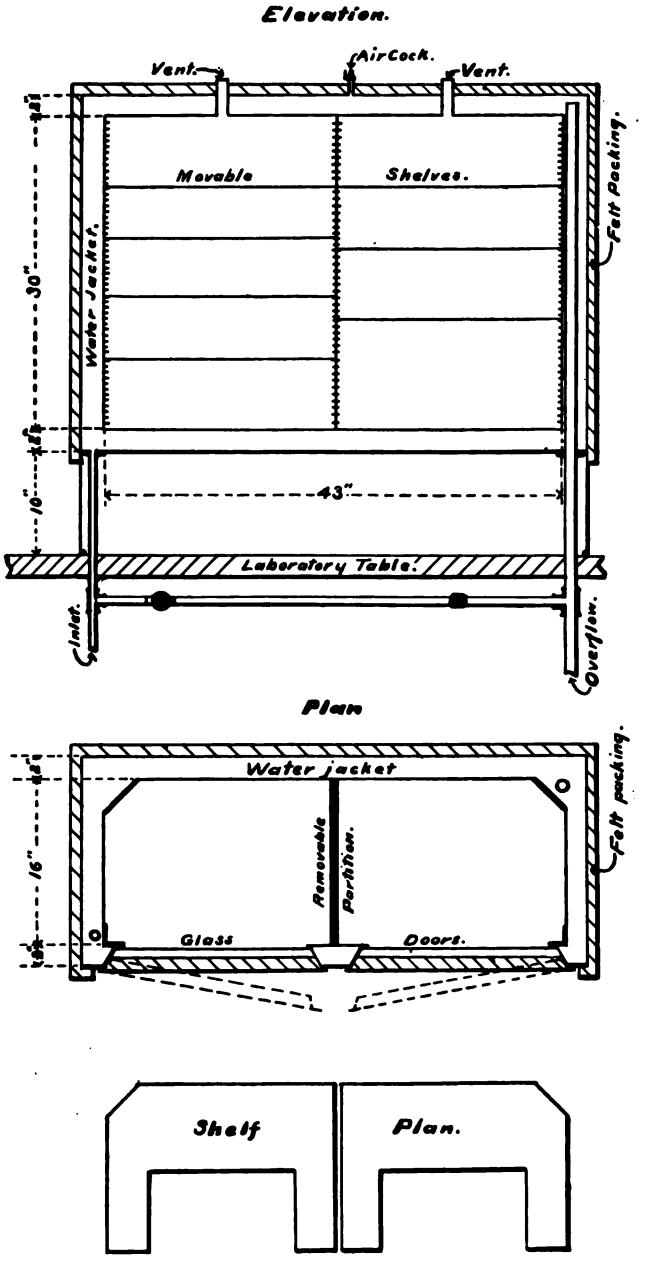


FIG. 7. — INCUBATOR FOR 20° C. WORK AT THE LAWRENCE EXPERIMENT STATION

or two, using a bottle or flask for the alcohol reservoir, a small pinchcock for the by-pass, and glass and rubber tubing for the other connections, in case brass fittings are not at hand. If brass or glass T's are not available, emergency ones may be made by cutting a small hole in the side of a piece of heavy rubber tubing and inserting a piece of glass tubing, with one end upset to form a wide lip. If the glass tubing is slightly larger than the hole in the rubber, the joint will be perfectly tight when new, and will answer for ordinary gas connections or even for water under low pressure.

A Wash Bottle for Sterile Water.—In certain procedures it is necessary to wash samples with sterile water. For this purpose the wash bottle shown in Figure 6 is easily made, and has done good service in the shellfish investigations previously mentioned. This consists of a half-gallon bottle fitted with a two-hole rubber stopper, through which pass a thistle tube plugged with cotton and a syphon of glass and rubber. The discharge end of the syphon passes through a rubber stopper in the neck of a small bottle from which the bottom has been removed, the tip being located well up inside the small bottle, where it is protected from contamination during use. A pressure pinchcock placed close to the small bottle enables the operator to regulate the flow and direct the stream of water with one hand, leaving the other hand free to hold the sample. By plugging the bottom of the small bottle with cotton and coiling the rubber tube about the large bottle, the whole apparatus may be sterilized in the autoclave without difficulty.

Twenty-degree Incubator.—In 1903 a large incubator was built for the 20° work at Lawrence which embodies some features not generally found in apparatus of this kind. The incubating chamber is surrounded by a water-jacket so designed that a constant circulation of water may be maintained, the water entering at the lower front left-hand corner, flowing completely around the incubating chamber to an overflow diagonally opposite, the flow of water being controlled by a stopcock with a graduated scale (not shown in cut) placed on the inlet pipe. A by-pass connecting the inlet with the waste pipe permits the water-jacket to be drained by opening a valve, both water valves being placed below the table on which the incubator stands, where they are easily accessible. The walls of the water-jacket are of heavy tinned copper, strongly cross-braced to prevent bulging, all joints being double-seamed and filled with solder for additional strength. The water-jacket is insulated by a thick layer of non-absorbent felt, covered by an outer casing

of galvanized iron, this outer casing being made in sections and fastened by screws, in order that the insulation may be readily removed and repairs made should occasion arise. Double doors are provided, the outer packed with felt and the inner of glass through which the contents of the incubator may be inspected without disturbing the temperature. Both inner and outer doors are fitted with piano hinges and heavy cleat catches. The outside finish is of dead black enamel, except the doors, which are of dull copper, and the trimmings, which are of lacquered brass. The incubation chamber is divided into two compartments by a perforated partition, each compartment having a capacity for about 1,000 standard size Petri dishes or thirty-six baskets of test tubes. The shelves are arranged around three sides of each compartment for convenience in getting at the contents and to allow space for tall apparatus, and are adjustable for height, being supported at one end by lugs on the partition, and on the opposite corners by cleated racks. The central partition, shelves, and shelf-supports are all removable, leaving the walls of the incubating chamber clear for cleaning or sterilizing, if necessary. The details of construction are shown in Figure 7.

A number of devices have been suggested for controlling the temperature of large incubators operated at 20° C., but these were considered either too complicated or too expensive to install and operate. Attempts were made at first to regulate the temperature of this incubator by passing the inflowing water through a coil heated by a gas burner, the flame of which was controlled by a thermo-regulator inside the incubator. This apparatus, while simple and perfect in theory, did not work well in practice, and was abandoned after about a year's trial for the present method of control. This consists of a gas burner placed directly under the incubator, connected with a Roux thermo-regulator. During hot weather a circulation of water from the city pipes is maintained sufficient to keep the temperature down within the limits at which the thermo-regulator can act, the amount of water flowing through the system being regulated by hand, and the exact temperature being controlled by the automatic regulator and gas flame. With an inspection morning and night, this method of control has proved fairly satisfactory, and a temperature of 20° C. has been maintained with a fluctuation of not over 1°. Fortunately the temperature of the city water never runs as high as 20° C., otherwise it would be necessary to pass it through an ice coil before admitting it to the incubator.

BOOK REVIEWS

Tables for Engineers and Architects[1]

This very useful set of tables contains in the revised edition, in addition to the tables given in the previous edition, the following:

A 5-place table of logarithms;

A 5-place table of logarithmic sines and tangents varying by 10 seconds from 0° to 3°, and of cosines and cotangents varying by 10 seconds from 87° to 90°;

A complete table of logarithmic trigonometric functions varying by minutes;

A table of natural trigonometric functions varying by 10 minutes;

A collection of trigonometric formulæ; and a table of decimal equivalents of inches, expressed in feet.

The old portion of the tables has been revised and enlarged to contain tables of logarithms of feet, inches, and fractions of an inch, varying by 1/32 of an inch from 0 to 50 feet, and by 1/16 of an inch from 50 to 100 feet; and parallel with these, the squares of these distances. This table is very useful in mensuration, and also particularly in the solution of triangles for figuring the data required for structural detail drawings in which it is necessary to get the precise lengths of diagonal members. The table of squares of distances, as well as the table of logarithms, is frequently very useful, and in some cases the logarithm and the square are both useful for the solution of the problem.

The book also contains the angles and logarithmic functions corresponding to different so-called bevels, the bevel being the height of a right-angled triangle which has a base of 12 inches. This table, also, is of great usefulness in structural computations: for instance, for a right-angled triangle, if one side is given and the slope of the hypothenuse, the other side may be quickly found.

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[1] Smoley's Tables: Parallel Tables of Logarithms and Squares for Engineers, Architects, and Students. By Constantine Smoley, C.E. 5th edition revised. New York: The Engineering News Publishing Co.

The previous edition contained the table of logarithms and squares only up to 50 feet. In the present edition, as already stated, this table has been continued to 100 feet. In this edition, also, there has been added a multiplication table for rivet spacing which is very convenient in the designing of rivet work.

The book will be found very useful by structural designers.

G. F. S.

Graphical Determination of Earth Slopes, Retaining Walls, and Dams[1]

Graphical methods are found valuable for many purposes, and this treatise sets forth their application to earth pressures and to retaining walls, structures designed to resist these pressures, but also includes dams, which can logically be treated in the same connection. The book is intended for the use of students rather than engineers in practice, and is purposely made less complete in the elaborate discussion of theories than would otherwise be the case.

The author has found, as might be expected, that the results obtained by graphical methods compare satisfactorily with those analytically obtained. In fact, earth pressures would appear a very suitable field for graphical treatment, since our knowledge of the data involved does not justify great precision in results. It is interesting to note that for the analytical theories considered, recourse is had to Rankine, that wonderful mathematician who has ably treated so many engineering subjects that it is never out of place to consult his books, however ancient they may seem.

The graphical methods used are largely those of Culmann, Rebhann, Weyrauch, and Blanc, and the book is thus mainly a compilation, or rather an adaptation, than it is a purely original treatise, although we must except the graphical determination of earth slopes of uniform stability.

The author apparently has had the opportunity to use more or less of this treatise with his students at Manhattan College, an advantage which tends to secure clearness of presentation. Although prepared

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[1] **Graphical Determination of Earth Slopes, Retaining Walls, and Dams. By Charles Prelini. New York: D. Van Nostrand Co., 1908. 129 + v pp., 75 il., 8vo.**

primarily for students of engineering, practicing engineers who have not specially pursued this subject elsewhere may readily find this book interesting and instructive.

Chapter I deals with the stability of earth slopes.

Chapter II with retaining walls by graphical methods.

Chapter III the same by analytical methods.

Chapter IV takes up the design of retaining walls.

Chapter V adds dams or walls subjected to water pressure.

In its typographical and mechanical make-up the book is satisfactory.

Highway Bridges[1]

In this rather elaborate work the author attempts to cover a wide field, treating not only of the computation of stresses on simple trusses, but carrying this as far as the treatment of the arch without hinges; also covering the design of highway bridges of wood, steel, stone, concrete, and reënforced concrete, as well as of piers, abutments, culverts, etc.

Part I treats of the stresses in steel bridges, both for highways and railways, from the simple beam to rather complicated but usual truss forms. Stresses in pins and in other minor parts, in portals and lateral systems, are taken up, and a large number of problems given to illustrate. Some of these last might as well have been omitted, as, for instance, the determination of dead stresses graphically, which method probably nobody familiar with analytical methods would ever use.

Part II treats of the design of highway bridges of all kinds and materials, giving specifications, detail drawings, and tables of weights, costs, etc.

We cannot but wish that the author had confined himself to a smaller field, and had treated some parts more fully. The book is somewhat lacking in balance, some parts being rather sketchy, while others are treated in too much detail. Nevertheless, it contains much valuable information, and will no doubt be useful to many engineers who have mainly to do with highway bridges. It is well printed and illustrated, and bears the marks of careful preparation. G. F. S.

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[1] The Design of Highway Bridges and the Calculation of the Stresses in Bridge Trusses. By Milo S. Ketchum. New York: Engineering News Publishing Co., 1908.

HYDRAULICS [1]

THIS work is one which every teacher of hydraulics will wish to have upon his shelves as a reference book, but as a text-book for use in American engineering schools it will probably not have a very extended use.

The first half, that dealing with hydraulics proper, takes up all of the topics usually discussed in such a work, but more than the usual amount of space is devoted to the physical properties of water and the motion of fluids. The equations for the latter are developed in a manner which is probably beyond the student of ordinary mathematical ability. The same may perhaps be said of certain other portions of the work, and for this reason it will not appeal, as it should, to many students of the subject in this country.

In the first chapter are discussed the physical properties of water, including cohesion, adhesion, capillarity, surface tension, and viscosity.

Chapter II, hydrostatics, takes up the usual propositions of this topic, as well as the equilibrium and oscillation of floating bodies.

In Chapter III the motion of water is considered, including vortex motion.

Then follow in order the flow through orifices, mouthpieces, and over weirs; fluid friction, the resistance and propulsion of ships; flow in pipes, including branches, and water hammer.

Uniform and non-uniform flow in open channels and stream gagings are covered in Chapter IX, and Chapter X closes the first portion with a discussion of the impulse of jets, pressures on vanes, etc.

The foregoing discussions are both interesting and satisfactory, but there is some unevenness of treatment. Weirs, for example, are allotted their due proportion of space, but there is less originality of method than is shown in many places.

Stream gagings, on the contrary, are cut short with a bare dozen pages, whereas this subject deserves much more attention in a work so comprehensive.

Chapters XI–XIX cover the applications of hydraulic principles to machinery. A brief discussion of the older forms of water wheels introduces the study of the modern forms of turbines. The American type of wheel receives rather brief notice, but, on the whole, present

[1] **Hydraulics and Its Applications. By A. H. Gibson. New York: D. Van Nostrand Co.**

practice is well set forth. The discussion of the theory of turbines is based upon the relations of the moment of momentum.

Losses of energy in the wheels are considered at some length, and the effects of standpipe and fly-wheel regulation are touched upon, though regulation, on the whole, receives too little attention.

Pumps, both reciprocating and centrifugal, are considered at length, and the latter are illustrated by the latest types.

The ram, air lift pump, and hydraulic air compression are considered in a short chapter, number XVII; number XVIII treats of meters and hydraulic power transmission; while the concluding chapter deals with jacks, cranes, presses, etc.

Four brief tables comprise the appendix.

The applications are well chosen and, if not described in sufficient detail for the practicing engineer, the students' needs are fully met, and more matter could probably not be introduced with advantage for teaching purposes.

The book contains over 700 pages, and is too heavy to be convenient. The type is large and clear, and the diagrams, of which there are many, are good, in striking contrast to those in another recent English work. The book is an excellent one and should do much to put the teaching of hydraulics upon a higher plane, from the theoretical side, making up in this way what it may lack as a handbook for the practicing engineer.

W. E. M.

Water-Power Engineering[1]

Into this bulky volume of nearly eight hundred pages, Professor Mead has gathered a large amount of information relating to the subject of water power. There has hitherto been no lack of literature bearing upon the many questions involved in the design of a modern water power plant—stream flow and storage, controlling works and power houses, turbines and governing devices—but this matter is widely scattered through technical magazines, professional reports, and engineering society publications. In gathering this information together and presenting its substance in a single volume, the author has rendered a distinct service to the engineering profession.

[1] Water-Power Engineering. By Daniel W. Mead. New York: McGraw Publishing Co. Price, $6.00.

Beginning in Chapter I with a brief historical review of the subject, in the next four chapters are discussed the more general questions of energy and water power, together with so much of hydraulic theory as relates to the flow of water in penstocks, flumes, and over weirs. The backwater curve also receives attention at this point. Chapters VI–XI deal with rainfall, run-off, and the measurement of stream flow.

Then follow five chapters on water wheels, their theory, construction, testing, and such considerations as influence the selection of a turbine for particular duties.

Chapter XVII takes up the load curve and its influence upon the design of a power plant.

Speed regulation and governors are fully discussed in the two following chapters and an appendix.

The arrangement and setting of turbines, power house design, head works and dams, including appendages to the same, together with numerous examples from recent constructions, are discussed in Chapters XX–XXV. Chapter XXVI deals with pondage and storage, number XXVII with the cost, value, and sale of power; and in the concluding chapter is given a brief outline of the proper scope for a report upon a water power project.

In the eight appendixes are given more detailed discussions of some of the points presented earlier in the work and numerous tables of the results of wheel tests, as well as stream flow data.

The book is presumably written for the use of advanced students in engineering courses, and it will serve admirably to place before such students the complexity and interrelation of the problems which enter into power plant design. Nevertheless, practice rather than theory is ever uppermost in the book, which throughout bears evidence of the author's familiarity with the best practice of the day and a desire to present to his students the essentials only. Graphical methods are extensively introduced throughout the book, notably in considering stream flow, storage, and turbine performance; several of these diagrams will doubtless be quite new to the profession.

It is to this feature of the book that it owes its strongest claims to originality. If some of the topics are discussed rather briefly, their broad scope may be sufficient justification, and the reader who wishes more detail will find at the end of nearly every chapter a most valuable list of references to the literature of the subject discussed therein.

One misses in a work so comprehensive anything more than a passing

reference to the question of water rights and damages for diversion, etc. The arrangement of the subject-matter as a whole would seem to be susceptible of some improvement, following perhaps a more natural order, as indicated in Chapter XXVIII.

The book is very fully and, on the whole, well illustrated. The indexing is good, the paper and press work satisfactory. In such a large work some errors are to be expected in the first edition; but there are occasional evidences of hurried proofreading, as, for instance, in Table LIV, page 661, where the costs of fuel per kilowatt hour are given as fractions of dollars instead of cents. The same error occurs in other columns.

The work is a distinct contribution to the literature of the subject, and will be read with interest and profit by any one engaged in the important field of water-power engineering. W. E. M.

Design of Chemical Laboratories[1]

This contains much of the material found in the early chapters of books on quantitative analysis, together with the results of the author's reading and experience; a useful feature is the designation of sources of supply.

Cement concrete—as might be expected—has even found its way into the laboratory, directions being given for the preparation of foundations for balances and floors for hoods; the reviewer thinks the imbedding of pipes and joints in concrete of doubtful expediency, twenty-five years' experience having shown the value of being able to get at every inch of piping with the tongs. Regarding foundations for balances, unless there be heavy machinery in operation in the building, there is no need of brick or concrete piers; unless the building be of wood, wooden shelves can be solidly fastened to the brick walls. One searches in vain for hardened filters, and for the materials out of which laboratory desk tops and shelves are made; nor is any mention made of the use of sand or "soda water" in extinguishing laboratory fires or the employment of chloride of calcium or sulphuric acid in balance cases when weighing hygroscopic substances.

[1] The Design and Equipment of Small Chemical Laboratories. By Richard K. Meade. Chicago: Chemical Engineering Publishing Co., 1908. 138 pp., 8vo.

It should be noted that the *agate mortar does contaminate the sample,* as Hempel has shown, and also that red rubber tubing is not as durable as the gray or zinc-filled rubber. The necessity of having the weights in constant use adjusted at least annually, and of even checking government certified apparatus, should be emphasized, as the writer has known of three cases in which this certification of apparatus was incorrectly done.

The author modestly hints that the work is intended for the young chemist, but it is a book from which even the old ones can learn something, and will be extremely useful to all those having to do with laboratories, whether chemical, physical, or biological. A. H. GILL.

THE VEGETABLE SOURCES OF DRUGS[1]

THE book is divided into two parts: Botany and Pharmacognosy.

The botanical part contains, first, a chapter giving in brief outline an account of the classification of the vegetable kingdom. Then follows a chapter on the anatomy of the higher plants, each organ being taken up separately, and this is followed by one on the histology of plants. Then comes a more detailed classification of the Angiosperms which yield vegetable drugs; after which is given a list of the medical plants found in cultivation.

These chapters dealing with so large a subject in so small a space necessarily treat the different parts briefly. This brevity of treatment is noticeable in the definitions, which are somewhat inadequate, especially the definitions of the words "morphology" and "ecology"; the word "habitat" is used incorrectly in place of "locality" or "geographical distribution"; and we note a casual reference to the hypothesis of the inheritance of acquired characteristics which would lead the student to assume that it was an accepted theory. It seems a pity that a more adequate classification has not been given, especially in the chapter on Angiosperms.

In the first chapter each group of plants is illustrated by certain well-known examples, and special stress is laid upon their different methods of reproduction. On the whole, the ground is fairly well covered. In

[1] A text-book of botany and pharmacognosy, by Henry Kraemer. Edition 3. Philadelphia: Lippincott, 1908.

some places a little fuller treatment would have been desirable, as, for example, it is rather a shock to find the yeasts placed without any qualification among the Ascomycetes, and if the division of the Basidiomycetes had been clearly shown it would make plainer the relationship of the mushrooms to the smuts and rusts.

In the chapter on the Angiosperms we note that the hemp, the fig, and the mulberry are placed together in one family, Moraceæ, without any suggestion that there is good authority for separating these types into three separate families. It is to be feared that the student studying this chapter will not have a very clear idea as to why various plants are placed in separate families and orders, as there is scarcely a hint of the characters by which these groups are separated. The definition of the poppy family is characteristic, "These are herbs with a milky or colored latex," which would apply equally well to the milkweeds.

Following these definitions, under each order, there is a more valuable account of the useful plants, with brief mention of the products obtained from them. These contain much interesting information. One small point that stuck the reviewer is that Chinese rice paper is not made from rice at all, but from the pith of a plant of the Ginseng family.

The second part of this work is probably more useful. It is divided into two chapters; the first on crude drugs, the second on the powdered vegetable drugs and foods.

The crude drugs are classified as seeds, roots, parts of roots and stems, flowers, fruits, leaves and herbs, exudations, juices, and other plant products.

Both chapters are intended to be used for the identification of drugs, and are supplied with artificial, or analytical, keys on the principle of works in systematic botany. The amount of detail in regard to each drug varies somewhat, but in general the name of the drug is followed by a statement of the name of the species and the organ from which it is derived. This is followed by a brief account of the geographical distribution of the species and the chief source of the commercial supplies.

Then follows a detailed description of the part used as the crude drug; next, a paragraph on its chemical constituents; third, a paragraph on the adulterants commonly used; and finally, a paragraph on allied drugs or plants.

The powdered drugs are classified into five groups by their color, greenish, yellowish, brownish, reddish, and whitish. These, in turn, are subdivided by various characteristics too numerous to mention. This

part of the work is well illustrated by figures, mostly drawn by the author, which will be a great help in identification. R. P. B.

Electrical Illuminating Engineering[1]

The recent developments in electric lamps of different types, together with the increasing prominence given to the subject of illuminating engineering, have created a demand for literature which gives a description of the modern electrical illuminants and which outlines the theory used and the methods of calculation employed in the design of a lighting system. The book in hand, prepared from notes used by the author in connection with his classes in illuminating engineering at Armour Institute, covers a very broad field in comparatively few pages, and as a result many points of considerable importance are either inadequately treated or entirely omitted. To be of use as a text in schools, the book should be supplemented to a large extent with lectures, as suggested in the preface. While some books now available on the subject of illuminating engineering may be criticised on account of the fact that they emphasize the particular product of some manufacturing company to too great an extent, this text is perhaps too impartial, and where several devices for accomplishing the same object are described there is little to aid one in deciding which is the most practical for any particular service.

The subject is introduced by brief chapters on light and color and on the units recommended for use in connection with illuminating engineering by the American Institute of Electrical Engineers. The next section deals with photometry and photometers, and is useful in that it brings together concise descriptions of the more recent types of photometers and illuminometers. This section would be greatly increased in its value to the reader if the practical application of the different types were discussed to a greater extent, and if some idea of the relative sensitiveness and accuracy of the different devices were given. The standards of illuminating power are treated from a historical standpoint, but particular attention is paid to the units now adapted by the various

[1] Electrical Illuminating Engineering. By William E. Barrows. New York: McGraw. 212 pp., il. Price, $2.00.

governments or national societies, and the valuable table of comparison of these units is included.

Electrical illuminants are considered under the heads of incandescent lamps, arc lamps, flaming-arc lamps, and vapor lamps. Owing to the limited amount of space devoted to these subjects there is very little descriptive matter included. The practical application of the different types of lamps is lacking. Several of the metallic filament lamps in either the experimental or commercial stage are mentioned, but there is little to aid one in determining which are or which may be employed to any great extent. Shades and reflectors are given some consideration, and the distribution curves of several of the better known types of reflectors are included.

The final chapter is devoted to the subject of illumination calculations. No new material is included in this chapter, but an attempt is made to present only such matter as will be of direct aid in calculating the illumination at a given point with the lighting sources known, or for determining the value of the light sources and their distribution when the illumination at any point is decided upon. Considerable attention is paid to the question of the arrangement of lamps for producing uniform illumination. The application of some of the formulas to specific forms of lighting could be profitably extended, and some discussion of the light reflected from the side walls and ceilings in certain installations might well be included.

There is little in the treatment of the subject that is original, but the book as a whole is valuable in that it brings together a great deal of the information desired by those interested in illuminating engineering and electric lamps. In order to apply this information intelligently in practical illumination problems, much more information than is included in the text is necessary. GEORGE C. SHAAD.

PUBLICATIONS[1]

Chemistry and Chemical Engineering

Henry Fay. — A Microscopic Investigation of Broken Steel Rails: Manganese Sulphide a Source of Danger. *Proceedings of American Society for Testing Materials*, 1908. il.

William Guertler. — Folgerungen für die Technik aus dem heutigen Stande unserer Erkenntnis des elektrischen Leitungswiderstandes der Metallegierungen. *Metallurgie*, Vol. 5, Heft 10. 5 p. 8vo.*

William Guertler. — Über die Verwendung von Rückstandsanalysen zur Festellung der Formeln von Metallverbindungen. *Metallurgie*, Vol. 5, Heft 6. 3 p. 8vo.*

William Guertler. — Bemerkungen zu dem Gesetz von Matthiessen, betr. den Temperaturkoeffizienten der elektrischen Leitfähigkeit der Metallegierungen. I. *Physikalische Zeitschrift*, Vol. 9, No. 1, pp. 29–36. 4 il. 4to.*

William Guertler. — Über die elektrische Leitfähigkeit der Legierungen und ihren Temperaturkoeffizienten. *Physikalische Zeitschrift*, Vol. 9, No. 12, pp. 404–405. 4to.*

William Guertler. — Stand der Forschung über die elektrische Leitfähigkeit der kristallisierten Metallegierungen. *Jahrbuch der Radioaktivität und Elektronik*, Bd. 5, Heft 1, pp. 17–81. 26 il. 8vo.*

William T. Hall and *George Defren.* — Text-Book of Physiological Chemistry in Thirty Lectures, translated from the German of Emil Abderhalden. New York: Wiley. 1908. 13 + 722 p. 8vo.*

F. J. Moore and *R. D. Gale.* — The Colored Salts of Schiff's Bases. — A Contribution to Our Knowledge of Color as Related to Chemical Constitution. *Technology Quarterly*, Vol. 21, No. 2, pp. 200–211. June, 1908. *Journal American Chemical Society*, Vol. 30, No. 3. March, 1908.*

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[1] In order that the extent of productive work carried on at the Institute may be better known, it is designed to publish a list of the publications of officers of the Institute, together with abstracts when possible. In this list the publications are arranged alphabetically by departments and then alphabetically by authors.

The asterisk after the title indicates that a copy of the publication has been placed in the library of the Institute.

F. J. Moore and *R. G. Woodbridge, Jr.* — The Colored Salts of Schiff's Bases, II — The Hydrochlorides of Bases Formed by Condensing *p*-Aminodiphenylamine with Aromatic Aldehydes. *Journal of American Chemical Society*, Vol. 30, No. 6, pp. 1001–1003. June, 1908.*

Arthur A. Noyes. — A Talk on Teaching. (Printed, not published.) 16 p.*

Arthur A. Noyes. — Address to New Students at the Massachusetts Institute of Technology. (Printed, not published.) 10 p.*

Ellen H. Richards. — Farm Home, a Centre of Social Progress. *Encyclopedia of American Agriculture*, Vol. 3.

Ellen H. Richards, E. M. Wade, R. N. Gilbert, C. E. Hanson, and *J. M. Talbot.* — Methods of Testing the Efficiency of Ventilation. *Technology Quarterly*, Vol. 21, No. 3. September, 1908.

Ellen H. Richards. — Cost of Cleanness. Fourth in the "Cost" Series. New York: Wiley. 1908. 104 p.

Ellen H. Richards. — Laboratory Notes on Industrial Water Analysis. New York: Wiley.

Ellen H. Richards. — Household Science in Elementary and Secondary Schools. *Proceedings of National Education Association*, June 29–July 3, 1908. Cleveland, Ohio.

H. P. Talbot. — Some Recent Investigations in the Chemical Department. *Technology Review*, Vol. 10, No. 4. 13 p.*

W. H. Walker. — The Relation of Chemistry to Street Railway Work. *Street Railway Bulletin*, Vol. 7, p. 134. 1908.

W. H. Walker. — Standard Methods of Analysis for Materials Used in Chrome-Tanning. *Journal American Leather Chemical Association*, Vol. 3, p. 267. 1908.

Civil Engineering

C. B. Breed and *George L. Hosmer.* — The Principles and Practice of Surveying. Vol. 2, Higher. New York. 1908. 432 p. 164 il. 8vo.

George E. Russell. — Notes on Hydraulics. Revised edition. Boston, September, 1908. 90 p.

The notes constitute the text for all students studying hydraulics at the Institute, save those of Course I, whose longer course has made it seem better that they should use a text and reference book. The notes are lithographed and form the nucleus of a larger and more comprehensive printed volume, which the writer hopes to publish in the near future.

Electrical Engineering

Dugald C. Jackson. — An Important Committee on Engineering Education. *Technology Review*, Vol. 10, pp. 276–280. July, 1908.

George C. Shaad. — Review of Barr's Direct-Current Electrical Engineering. *Science*, November 25, 1908.

Geology

Reginald A. Daly. — The Mechanics of Igneous Intrusion — Third Paper. *American Journal of Science*, Vol. 26, pp. 17–50. 8vo. July, 1908.

Reginald A. Daly. — The Origin of Augite, Andesite, and of Related Ultra-Basic Rocks. *Journal of Geology*, Vol. 16, pp. 401–421. Chicago, August, 1908.

H. W. Shimer. — Dwarf Faunas. *American Naturalist*, Vol. 42, pp 472–490. July, 1908.*

The first part of the article discusses the chief causes of the dwarfing of invertebrate water-living faunas, using recent examples as illustrations; the second part considers some fossil examples with their probable causes. The chief agency is shown to be an abnormal habitat A species, for generations used to an environment of sea water with a certain unvarying density, temperature, clearness, and depth, would become so accustomed to that state of affairs that a change in one or more of the factors would affect it unfavorably.

The chief causes of dwarfing are suggested as being: (1) a change in the normal chemical content of the water; (2) the presence of mechanical impurities in the water; (3) a floating habitat; (4) variations in temperature; (5) extremes in depth of water.

H. W. Shimer. — The Pennsylvania-German as Geologist and Paleontologist. *The Pennsylvania-German*, Vol. 9, pp. 411–414. September, 1908.

The first part briefly discusses the character of the Pennsylvania-German colonists and the environment amid which they developed in this country, with the resultant type so well known from New Jersey and New York to Illinois. The second part gives a very brief biography of some of the geologists and paleontologists derived from this stock.

Mathematics

E. B. Wilson. — The Equilibrium of a Heavy Homogeneous Chain in a Uniformly Rotating Plane. *Annals of Mathematics*, Second Series, Vol. 9, No. 3, pp. 99–114. April, 1908.*

The exact solution of the problem of the figure of equilibrium of a heavy homogeneous chain in a uniformly rotating plane is apparently not to be obtained in finite form in terms of the known functions of mathematics. As the problem is one of interest, an approximate solution, therefore, seems worth while. It is this that is given in the above paper. The chief fact of physical interest is that for a given chain endowed with a given angular velocity there are a finite number of distinct positions of equilibrium which differ in the number of loops and nodes which the chain may have. There are also points of mathematical interest in connection with the approximations introduced in the solution.

E. B. Wilson. — Logic and the Continuum. *Bulletin of the American Mathematical Society.* Second Series, Vol. 14, No. 9, pp. 432–443. June, 1908.*

The article on logic and the continuum contains a critical discussion of some fundamental principles of mathematical logic which have been developed by E. V. Huntington and others, and which appear not to have acquired their merited place in discussions of the subject. These matters are then applied to the treatment of the continuum with especial reference to Zermelo's alleged proof of the possibility of well-ordering the continuum. The principal conclusion is that Zermelo bases his proof on an axiom which is more transcendent than the theorem he wishes to prove.

E. B. Wilson. — On the Principle of Relativity. *Philosophical Magazine,* pp. 419–422. September, 1908.*

The short note on the principle of relativity is in reference to a new principle of relativity for electrodynamics recently propounded by Bucherer. From a cursory examination of Bucherer's chief formula, it appears that neither his principle nor any one like it is likely to meet with favor as the ultimate foundation of electromagnetism. It may be added that we understand that he has now abandoned his principle and adopted the Lorentz-Einstein hypothesis.

Mining Engineering and Metallurgy

H. O. Hofman. — Recent Improvements in Lead Smelting. *Mineral Industry,* Vol. 16, pp. 657–693. 1907.

H. O. Hofman. — Review of A. G. Bett's Lead Refining by Electrolysis. *American Chemical Journal,* Vol. 40, p. 493. 1908.

R. H. Richards and *C. E. Locke.* — Progress in Gold Milling in 1907. *Mineral Industry,* Vol. 16, pp. 553–566. il. 8vo. 1908.

R. H. Richards and *C. E. Locke.* — Progress in Ore Dressing and Coal Washing in 1907. *Mineral Industry,* Vol. 16, pp. 960–1014. il. 8vo. 1908.

Modern Languages

John Bigelow, Jr. — Review of Trevelyan's "The American Revolution." *American Historical Review*, Vol. 13, pp. 874–875. New York, July, 1908.

John Bigelow, Jr. — The Saber and the Cavalry. Fort Leavenworth, Kansas. *Journal of United States Cavalry Association*, Vol. 19. 7 p. April, 1908.

Naval Architecture

W. Hovgaard. — A Proposed New Type of Conning-Tower for Large Battleships. *Jane's "Fighting Ships,"* for 1908, pp. 419–424. il. London.*

This is an account of recent war experiences and firing experiments, showing necessity of improvements in conning-towers, with a critical description of existing conning-towers, pointing out existing defects, and an exposition of the general principles governing the design, followed by a description of proposed location and construction of conning-towers.

W. Hovgaard. — An Analysis of the Resistance of Ships (a paper read before Institution of Naval Architects, London). *Transactions Institution of Naval Architects*, London, Vol. 50, pp. 205–222. il. April 10, 1908.

This contains general form of the mathematical expression for wave-making resistance and some remarks respecting the formation of ship waves. There is also a discussion of the form of three terms of the expression for wave-making resistance, namely, the speed term, the term involving the principal dimensions, and the term involving the fineness.

This discussion is based on an analysis of the published curves of resistance, notably those of serial experiments made by the older and younger Froude in England, by Colonel Rota in Italy, and by Naval Constructor Taylor in the United States.

In the appendix is given an explanation of the method of focal diagrams used in the analysis of the curves, together with more detailed description of the analysis.

The paper is accompanied by several plates, which show curves of resistance, focal diagrams, etc., and a table giving a summary of results.

Physics

Daniel F. Comstock. — The Indestructibility of Matter and the Absence of Exact Relations among the Atomic Weights. *Journal American Chemical Society*, Vol. 30, pp. 683–688. May, 1908.

Louis Derr. — Photography for Students of Physics and Chemistry. New York: Macmillan. 1906.

R. A. Millikan and *John Mills.* — Electricity, Sound and Light. Boston: Ginn & Co. 1908. 8vo.

Institute Publications

Massachusetts Institute of Technology. — Bulletin, Vol. 43, No. 4, Programme. Edited by Dana P. Bartlett. Boston, June, 1908. 381 p.*

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